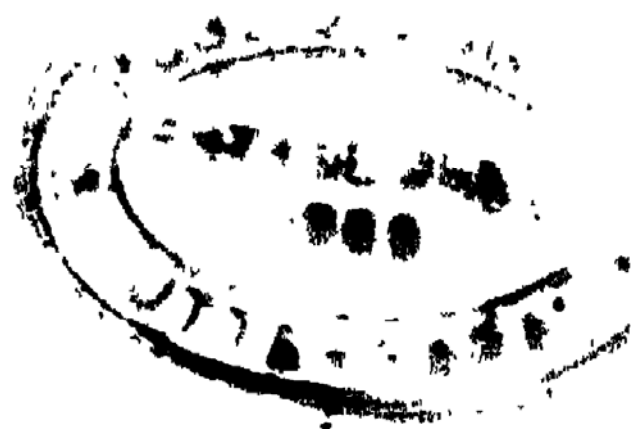


A MANUAL OF INORGANIC CHEMISTRY



**BY
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PART I.

GENERAL PRINCIPLES.

CHAPTER I.

INTRODUCTION.

Three Forms of Matter.—Substances are met with in nature in three forms, viz., *Solid*, *Liquid*, and *Gas*. Any one of these three forms of matter can often be converted into another, and most substances can exist in more than one of these three forms. In this transformation or conversion of matter, heat is the chief agent. Thus, water when heated becomes steam, and when cooled (*i.e.* deprived of heat) becomes solid ice. So if we heat ordinary sulphur, it will first become a thick liquid which on further heating will be changed into brown vapours. All gases can be liquefied, and all liquids solidified. In so doing we have not only to cool the substance, but in some cases we have also to subject it to very great pressure. It should be noted that in this change of states of matter the essential nature of the thing is not altered. The transformed substance reverts to its original state when the conditions are reversed.

Physical and Chemical Changes.—When we look around us we observe frequent changes taking place in things: these changes are regarded as of two kinds, viz., *Physical* and *Chemical*. Thus, when water is heated it is changed into steam, and when cooled it becomes ice; iron when heated becomes 'red-hot' and afterwards 'white-hot', emitting light; a piece of steel when rubbed with a magnet attracts other pieces of iron; a glass rod is electrified when rubbed with silk. These changes

produced in the substances are called *physical*: they do not affect the composition of the things; the essential nature of the substances remains unaltered, and the substances may easily be made to return to their original state. But when the white of egg is changed by heat into solid albumen, or anything burns in air, or organic bodies undergo putrefaction,—the changes produced are *chemical*: they alter the composition or essential nature of the things which cannot easily or cannot at all be brought back to their former state.

The science which deals with physical changes is broadly called Physics, while the science which studies chemical changes is called Chemistry. These changes, though they are distinct from each other, are closely related. Chemical changes are in many cases followed by physical changes. Thus, in the case of the steam-engine, the burning of coal is a chemical change, but the heat produced thereby converts water into steam which in expanding imparts motion to the engine.

~ Conservation of Mass or Indestructibility of Matter.—In all the changes that take place in the universe two principles are involved, viz., (1) that 'energy is never lost' and (2) that 'matter can never be created or destroyed'. The first principle is assumed in Physics (including Kinetics, Mechanics, &c.), and the second principle forms the foundation of the science of Chemistry.

The principle of Conservation of Mass or Indestructibility of Matter simply states that we can neither create nor destroy a particle of matter, we can only alter its form. It asserts that *'the quantity of matter which takes part in a chemical change remains unaltered when that change is completed'*; in other words, that *in a chemical change there is neither gain nor loss of matter*. At first sight it might appear, for example, that when coal or candle burns, it is utterly destroyed, no new substance being produced in its place. But the fact is that in these cases nothing is lost. This will be evident from the following experiments.

1. Take a large flask and place in it one or two pieces of phosphorus. Close the mouth of the flask with an air-tight cork, and weigh the whole apparatus. Next, carefully heat the flask: the phosphorus will burn. After the apparatus has cooled down, weight it again. The weights in the two cases will be found to be equal to each other.

2. Take a wide glass tube or chimney, and close its lower end with a perforated cork. Place a candle on the cork, inside the chimney. Connect, by means of corks and tubes, the chimney A

with (1) a flask B containing lime-water and (2) a U-tube C containing caustic soda or caustic potash. Carefully weigh the apparatus ABC as fitted up. Then connect the

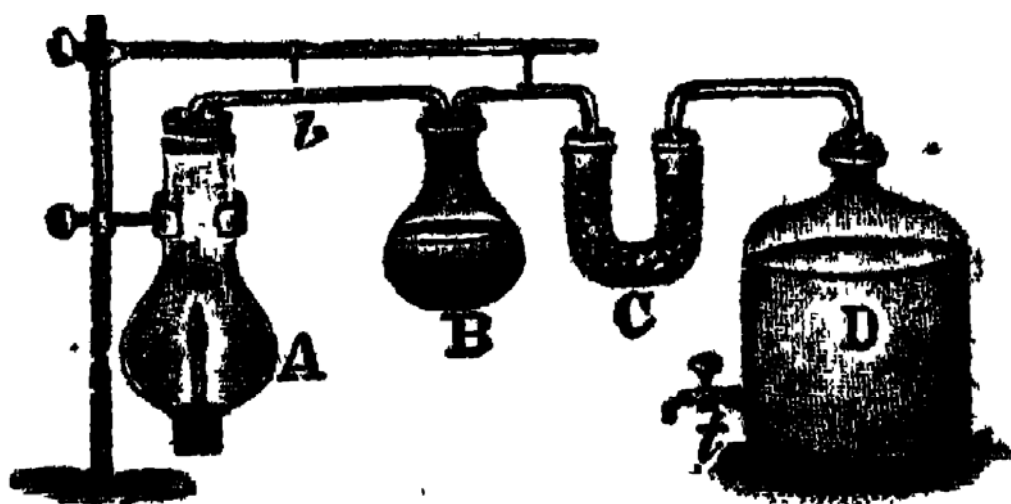


Fig. 1.

U-tube with a bottle D containing water which may be drawn out by the tap *t*. [This arrangement by which air can be drawn through the apparatus is called an *aspirator*]. Now light the candle and open the tap *t*. As the water runs out, a partial vacuum is produced in the bottle D, and so air (which keeps the candle burning) enters into the apparatus through the ~~bores~~ in the cork. After the candle has burned for some time, close the tap—the flame will be extinguished—and disconnect the U-tube with the bottle D. Now weigh again the apparatus ABC. The apparatus will be found to have *increased* in weight. Hence we conclude, *when anything burns there is no loss of matter*.

NOTE.—In the above experiment observe the following :

(1) Small drops of water collect in the inside of the cool tube *b*. This water is produced by the union of oxygen (of the air) with the hydrogen contained in the candle.

(2) The limewater in the flask B is turned milky. This is caused by the carbon dioxide which is formed by the union of the oxygen (of the air) with the carbon (of the candle).

(3) The caustic potash or soda contained in C has increased in weight ; because, the substance has absorbed the small quantities of water and carbon dioxide which have escaped through *b* and B.

(4) The increase in weight of the apparatus A B C, after the candle has burnt, is exactly equal to the quantity of the oxygen (of the air) used up.

* **Elements and Compounds.**—There are different kinds of substances in nature, and most of them are complex in character, being made up of two or more simpler substances. Accordingly chemists have divided substances into two broad classes, viz., Elements and Compounds. For example, water is a compound which is made up of (and can be split up into) the elements oxygen and hydrogen ; common salt is a compound of the elements sodium and chlorine. Gold, silver, iron, and other metals, oxygen, carbon, sulphur, &c. are examples of elements ; while sand, clay, candle, oils, animal and vegetable bodies are all compounds. Of the infinite number of substances in nature, about eighty are known to be elements, the rest are all compounds. *An Element is defined as a substance which has not been resolved or split up into simpler substances : while a Compound is a substance which contains two or more simpler substances (elements) united together in definite proportions, and which can therefore be broken up into two or more elements.*

List of Elements.—The following is an alphabetic list of the known elements. Of their total number, nearly half are important and commonly found in nature, the rest are more or less rare. At ordinary temperatures, ten of the elements are gases, viz., chlorine, fluorine, hydrogen, nitrogen, oxygen, argon, helium, krypton, neon, xenon. Two are liquids, viz., bromine and mercury. The rest are all solids.

In this list the names of non-metals (nineteen in number) are printed in capitals, and those of metals in ordinary types—

Aluminium	HELIUM	Rhodium
Antimony (Stibium)	HYDROGEN	Rubidium
ARGON	Indium	Ruthenium
Arsenic	IODINE	Samarium
Barium	Iridium	Scandium
Beryllium (Glucinum)	Iron (Ferrum)	SELENIUM
Bismuth	KRYPTON	SILICON
BORON	Lanthanum	Silver (Argentum)
BROMINE	Lead (Plumbum)	Sodium (Natrium)
Cadmium	Lithium	Strontium
Cæsium	Lutecium	SULPHUR
Calcium	Magnesium	Tantalum
CARBON	Manganese	TELLURIUM
Cerium	Mercury (Hydrargyrum)	Terbium
CHLORINE	Molybdenum	Thallium
Chromium	Neodymium	Thorium
Cobalt	NEON	Thulium
Columbium (Niobium)	Nickel	Tin (Stannum)
Copper (Cuprum)	NITROGEN	Titanium
Dysprosium	Osmium	Tungsten (Wolframium)
Erbium	OXYGEN	Uranium
Europium	Palladium	Vanadium
FLUORINE	PHOSPHORUS	XENON
Gadolinium	Platinum	Ytterbium
Gallium	Potassium (Kalium)	Yttrium
Germanium	Praseodymium	Zinc
Gold (Aurum)	Radium	Zirconium

Mechanical Mixture and Chemical Compound.—A compound substance must be distinguished from a mere mixture of two or more simpler substances. We may mix two or more substances in various proportions, but the mixtures will not necessarily be chemical compounds. The difference between a mechanical mixture and a chemical compound will be clear from the following experiments with iron and sulphur :

Mixture of Iron and Sulphur.

Let us mix together small quantities of powdered iron and sulphur. The mixture will contain the particles of iron and sulphur in close touch ; but the two substances will never combine or unite together, however intimately we may mix them. Thus—

Compound of Iron and Sulphur.

Let us make a mixture of 7 parts iron and 4 parts sulphur, and heat the mixture in a test tube. First the sulphur will melt and then the whole mass will glow. After the glowing has ceased and the mass has cooled, let us break the test tube and examine the

Mixture of Iron and Sulphur (cont.)

(1) If we examine the mixture with a lens or microscope, we shall detect the black particles of iron and yellow grains of sulphur ;

(2) If we shake a little of the mixture with water, the particles of iron and sulphur will separate as they settle down ;

(3) If we pass a magnet over the mixture, the magnet will attract the particles of iron ;

(4) If we pour carbon disulphide on the mixture and shake, the sulphur will be dissolved and the iron left behind.

Compound of Iron and Sulphur (cont.)

substance formed. It is a dark (bluish-black) mass resembling neither iron nor sulphur—

The iron or sulphur can no longer be discerned with the microscope, and the substances cannot be separated by means of water, or a magnet, or carbon disulphide.

In fact the iron and sulphur have combined chemically to form a homogeneous mass (called 'iron sulphide') whose properties are different from those of either iron or sulphur.

Hence, we may define a *Mechanical Mixture* as the result produced when different substances merely mingle together in any proportion, without losing their identity. The components of a mixture can be separated from each other by purely mechanical means.

On the other hand, a *Chemical Compound* is the substance formed by the union of different substances in definite proportions, and possessed of properties quite different from those of its constituents. The constituents of a compound cannot be discerned or separated by ordinary means.

4. **Chemical Action.**—It is the process by which change in the composition of a substance is brought about, or the process by which the particles of different substances are rearranged or redistributed. We measure chemical activity by the speed with which a change takes place, by the amount of heat evolved, or by the electric effects accompanying the change. These and similar other considerations lead us to regard particular substances as 'more or less active,' and to say that 'great or little chemical affinity (or attraction) subsists between any two subs-

tances.' If however we are asked—why chemical action takes place at all—we cannot answer the question. We are as much ignorant of the cause of chemical action as of the cause of gravitation.

The characteristics of chemical action are these:—

(1) In a chemical change there is no gain or loss of matter.
(2) Substances obtained as the result of chemical action differ widely from those which produce them.

(3) Chemical action always takes place between fixed proportions of substances.

(4) Chemical action is attended with evolution or absorption of energy (usually in the form of heat). [Some compounds (*e. g.*, hydrogen iodide, nitrous oxide) in the formation of which heat is absorbed are called *endothermic*, as opposed to the majority of compounds, called *exothermic*, whose formation is attended with evolution of heat]. Light, explosion, and electricity may also be produced by chemical action.

Illustrations of Chemical Action: (1) *Burning or Heating in Air.*—Familiar instances of chemical action are met with when substances are burned or highly heated in air. The effects of heating some metals will serve as examples.

Let us weigh a piece of clean magnesium ribbon in a porcelain crucible with its lid, and heat the metal in the way represented in Fig. 2, often raising the lid so as to admit air, but not to allow the fumes to escape. When the metal has been converted into a white ash, we allow the crucible to cool down and then weigh it with its contents. *An increase in weight will be observed.*

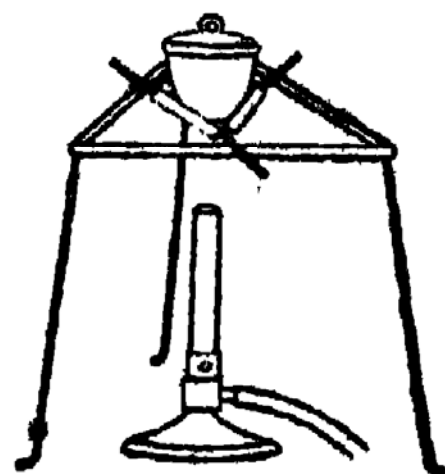


Fig. 2.

If we heat a piece of lead, zinc, or tin in the same way, stirring the melted mass with an iron-wire till a white powder is obtained, we shall find in each case that as a result of heating in air the metal gains in weight.

Lavoisier's experiments on Air.—The explanation of what takes place when substances are burnt or highly heated in air, was given by the French chemist Lavoisier who performed the following experiments. [The apparatus represented here are modifications of those used by him].

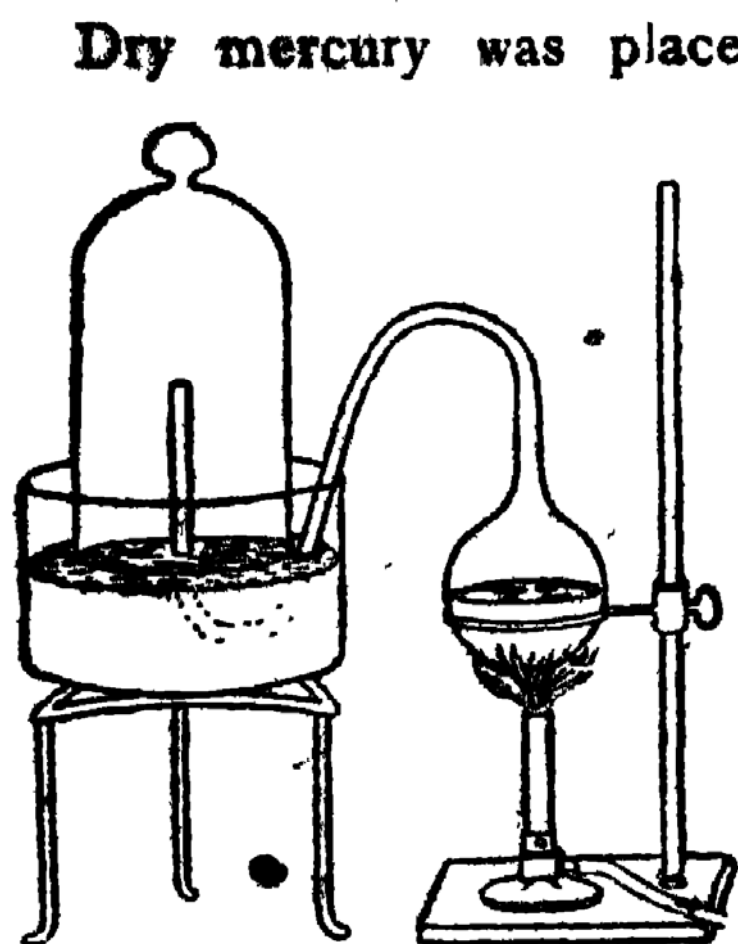


Fig. 3.

Dry mercury was placed in a globe or retort the neck of which was bent and passed into a bell-jar standing in a basin of mercury (Fig. 3). The volume of air in the retort and bell-jar having been measured, the mercury in the retort was heated. After heating for 12 days, it was found that a certain portion of the mercury had been changed into a red powder (called *calx* of mercury), and that the volume of

air had undergone a diminution of $\frac{1}{5}$ of its original volume. It was also noticed that the gas (called *azote* or *nitrogen*) left in the bell-jar did not allow substances to burn in it.

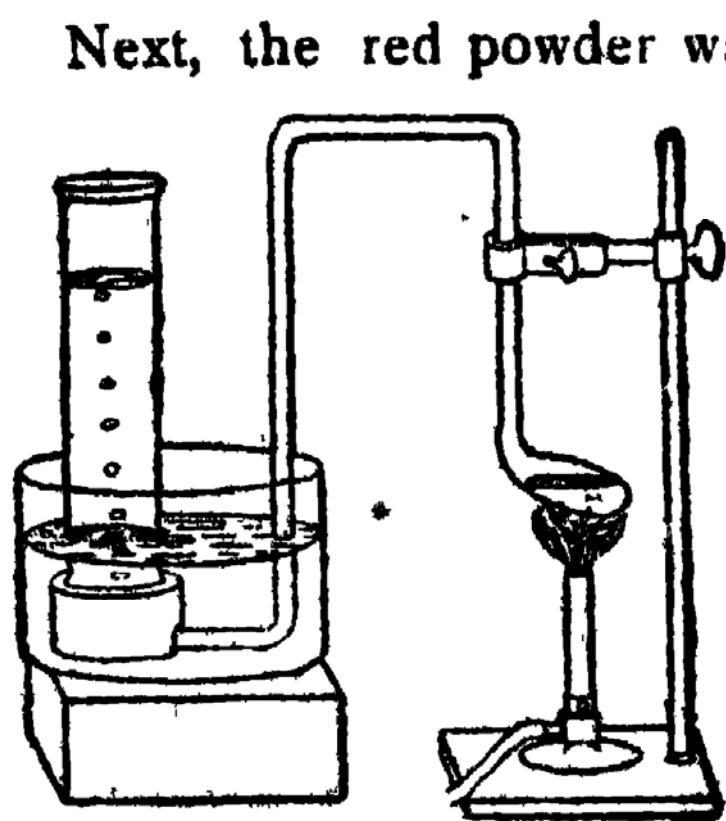


Fig. 4.

Next, the red powder was collected and strongly heated in a tube (Fig. 4). The red solid disappeared, giving place to (1) liquid mercury which condensed on the cool parts of the tube, and (2) a gas which being collected was found to be equal in volume to that which was lost by the air in the previous experiment. This gas (named *oxygen*) was found to be one in which substances

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burned brightly, and which being mixed with the gas left in the bell-jar gave ordinary air again.

These and similar other experiments proved that—

(i) *Air consists mainly of two gases, Oxygen and Nitrogen,—the former, comprising $\frac{1}{5}$ of the volume of air, is the supporter of combustion, and the latter forming the remaining $\frac{4}{5}$ is very inactive :*

(ii) *When a substance is changed by being burnt or highly heated in air, the change is due to the chemical union of the substance with Oxygen.*

(2) *Water is a compound of the gases Hydrogen and Oxygen : Electrolysis of Water.*—Water is a compound substance and can be broken up into its constituent elements by a current of electricity. This is demonstrated thus. In a glass basin, there are projected two platinum plates which can be connected with the two poles of a battery. Water is poured into the vessel, and some sulphuric acid is added (in order to render the water a conductor of electricity). Two glass tubes filled with the same acidulated water are then inverted over the platinum plates. On passing a current of electricity, the water is split up into its gaseous constituents, Hydrogen and Oxygen. The former, collecting in the tube over the negative plate, burns with a pale blue flame when a lighted taper is applied to it; while the latter, which collects over the positive plate, ignites a glowing chip of wood. The volume of the hydrogen is also seen to be double of that of the oxygen.

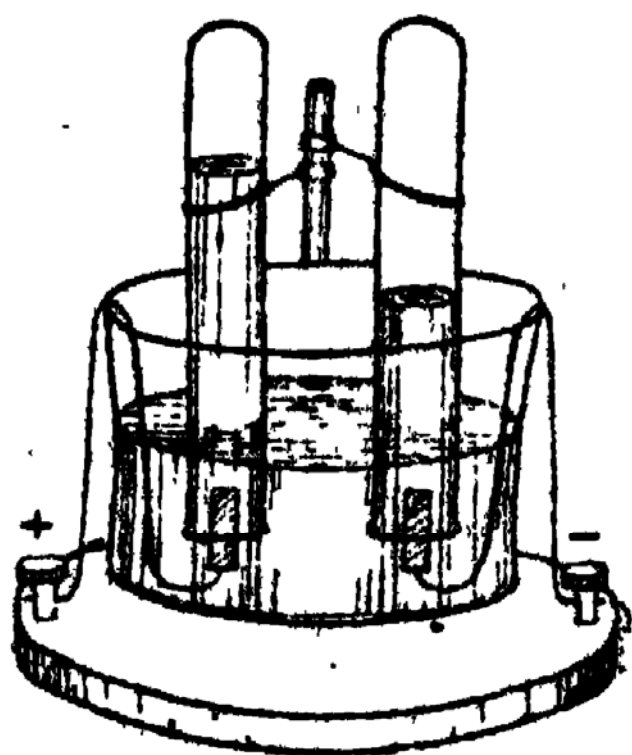


Fig. 5.

The Action of Zinc on a diluted Acid.—Some granulated zinc is placed in a flask which is fitted up with a thistle-funnel and connected with a U-tube containing calcium chloride. To the other end of the U-tube is attached another tube drawn out to a jet. On gradually pouring dilute hydrochloric or sulphuric acid down the funnel, hydrogen gas is evolved: the gas is deprived of moisture by the calcium chloride and escapes through the jet. After a few minutes, when the gas has swept all the air out of the apparatus, it may be lighted at the jet. If now a dry glass tube is held over the flame, minute drops of water will be seen to collect in

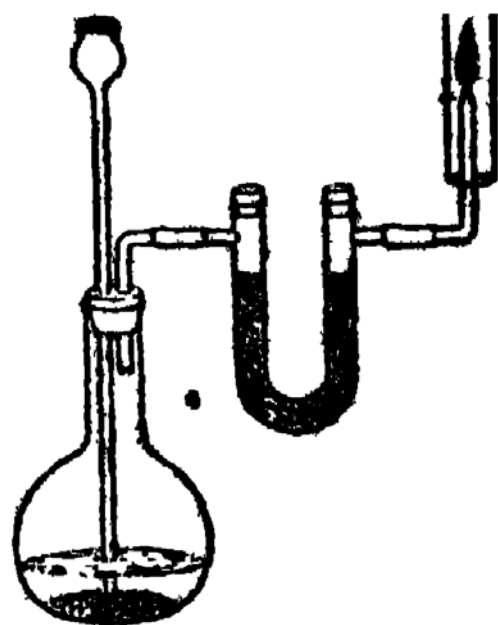


Fig. 6.

the cooler parts of the tube. This shows that when hydrogen burns in air (*i. e.* unites with oxygen), water is produced.

(3) Examples of Solution in water, and of Substitution of Metals.—1. Let us take a few crystals of sulphate or nitrate of copper, and dissolve them in water. If a clean piece of iron or zinc is now dipped in either of the solutions, it will soon be coated with a deposit of copper.

Again, a bright strip of copper becomes coated with mercury when it is placed in a solution of mercuric chloride. In these instances the immersed metal takes the place of the metal deposited, as will be seen by examining the solutions left after the changes.

2. Let us make solutions of mercuric chloride and potassium iodide, and then gradually add one solution to the other. Two new compounds will be formed, *viz.*, mercuric iodide (which is deposited as a red powder) and potassium chloride (which remains in the solution).

Similarly, when we add a solution containing silver nitrate to a solution containing one-third as much sodium chloride (common salt), the constituents of the compounds exchange

places, forming silver chloride and sodium nitrate. The former is insoluble in water and thus separates from the solution as a white powder.

Modes or Kinds of Chemical Action.—As the above experiments show, chemical action takes place in one of the following ways:—

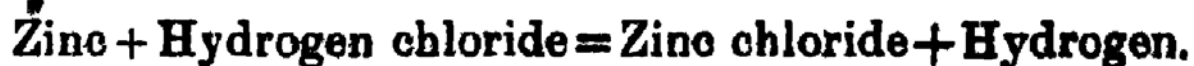
(1) **Combination or Synthesis.**—It is the process in which a compound substance is produced by the direct union of its constituents. Such are the union of iron and sulphur to form iron sulphide, the union of mercury and oxygen to form red oxide of mercury, and so forth.



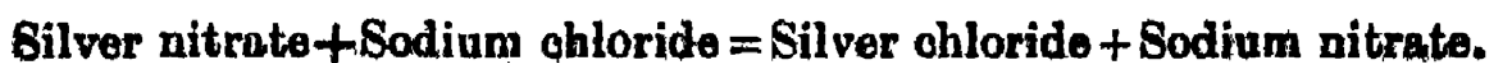
(2) **Decomposition or Analysis.**—It is the process in which a compound is broken up into its constituents, as when red oxide of mercury is decomposed into mercury and oxygen. *Electrolysis* is a special form of analysis in which a compound is resolved into its elements by means of an electric current: thus water is electrolyzed into hydrogen and oxygen.



(3) **Displacement or Replacement.**—This is the mode in which an element expels another from its compound and takes its place. Thus when zinc acts upon hydrochloric acid, it unites with the chlorine of the acid, setting hydrogen free. Iron displaces copper from a solution of copper sulphate.



(4) **Double Decomposition or Mutual Exchange.**—It is the process in which the constituent parts of two compounds change places. Thus when solutions of mercuric chloride and potassium iodide are mixed together, potassium chloride and mercuric iodide are formed. Similar is the interaction of silver nitrate and sodium chloride.



NOTE.—Another kind of chemical change is occasionally met with, specially in the case of organic compounds, when by mere

re-arrangement of particles one substance is changed into another which has different properties although the relative proportions of its constituents remain the same as before. This sort of transformation is called *Internal Rearrangement*.

Means or Conditions of Chemical Action.—The following are the means by which chemical changes are induced or brought about, and one or more of them are required in every case of chemical action:—

(1) **Contact.**—This is the most important condition of chemical action. In order that different substances (*e.g.*, zinc and sulphuric acid, hydrogen and oxygen) may unite, they must be in actual contact. For this reason, solids have often to be used in a finely divided or powdered condition.

(2) **Solution.**—When we have to bring about a chemical action between two or more solid substances, we take at least one of them in its liquid state (*i.e.*, we make a solution of it, or liquefy it by fusion). The reason is that the action between solids is slower than the action between a liquid and a solid.

(3) **Heat.**—In most cases heat expedites chemical action, and in some cases (as when mercuric oxide is decomposed into mercury and oxygen) heat alone causes chemical change.

There are some other agencies which sometimes induce or aid chemical action, *viz* —

(4) **Light.**—Thus chlorine and hydrogen at once combine when their mixture is exposed to light, but no action takes place when their mixture is kept in the dark.

(5) **Pressure.**—Thus lead sulphide is produced when a mixture of finely powdered lead and sulphur is subjected to enormous pressure. Gunpowder is exploded by percussion.

(6) **Electricity.**—Many compounds (*e.g.*, water) are decomposed by electric current. Again, electric sparks may sometimes bring about the combination of different elements.

(7) **Catalytic Agents.**—*i.e.*, certain substances which (though they do not themselves take part in the chemical change) help the action to a large extent. Such is manganese dioxide in

the preparation of oxygen from potassium chlorate. This obscure process by which chemical change occurs in the presence of substances which do not themselves appear to enter into combination, is called *induced action* or *catalysis*.

Definition of Chemistry.—"Chemistry is that science which treats of the composition of matter, of the changes produced therein by heat and other natural forces, and of the action and reaction of different kinds of matter on each other" (Jago). A knowledge of Chemistry enables us to understand the nature of things, to resolve compound substances into their elements, and to prepare complex substances from simpler ones.

Chemistry compared with Physics.—Chemistry is closely related with Physics. Both these sciences study the properties of substances; but they also differ in many respects:

(1) In Physics substances are divided into solids, liquids, and gases. In Chemistry substances are primarily classified into elements and compounds.

(2) Physics studies the universal properties of matter (*e. g.* density, hardness) and mere 'physical' changes, such as are produced by heat, electricity, &c. Chemistry studies the composition of substances and concerns itself with their analysis and synthesis.

University Examination Questions.

1. Explain what you understand by *Physical* and *Chemical* changes as affecting matter. Give examples. [C. 91].

2. Explain clearly the meaning of the statement that matter is indestructible. What evidence can be brought forward in support of the statement? [C. 07]. Describe, in detail, an experiment proving that there is no loss of matter in chemical changes, and make a sketch of the apparatus which you would use. [C. 1900, 1913].

Describe exactly how you would prove, by experiment, that water is produced when a candle (or the oil of a lamp) burns. What element is proved by this experiment to be present in the candle or oil? [C. 03.].

3. Define an *Element* and a *Compound*, and give an example of each [C. 92].
4. State the points of difference between a 'mixture' and a 'compound.' [C. 1915]. What is the difference between a mixture of two elements? Describe simple experiments in support of your explanation [C. 99, 08].
5. Describe briefly the different modes of chemical action. [C. 93]. Explain the term catalysis [C. 1911, 16; A. 1914], synthesis, analysis [C. 1910, 14], double decomposition [C. 08, 16].
6. Mention briefly the special conditions which aid or induce chemical changes and illustrate your reply by examples. [C. 91, 95].
7. Define Chemistry; and illustrate your definition by examples. [C. 96].

CHAPTER II.

PHYSICAL MEASUREMENTS.

The Metric System.—The system of measurements adopted in scientific works is the Metric System, in which the unit of length is the *metre*, the unit of volume is the *litre*, and the unit of weight is the *gram* (also spelt *gramme*). These three units are related to one another.

The prefixes used to denote fractions of these units are *deci* (=one-tenth), *centi* (=one hundredth), *milli* (=one-thousandth); the prefixes denoting multiples are *deca* (=10), *hecto* (=100), *kilo* (=1000). Thus, 1000 millimetres = 10 decimetres = 1 metre; 1 kilometre = 10 hectometres = 1000 metres, and so on. Similarly, 100 centilitres = 10 decilitres = 1 litre; 1 kilogram = 1000 grams = 100000 centigrams. The advantage of the metric system is that it involves only multiplications and divisions by 10 or multiples of 10.

The Unit of Length.—The *metre*, originally intended to be the ten-millionth part of a quadrant of the earth's meridian, is the distance between two marks on a certain rod of platinum kept in Paris. It is very nearly equal to 39.37 inches. Hence, 1 kilometre = 1093 yards.

The Unit of Volume.—The *litre* is the volume of a cube, each face of which is 1 square decimetre, *i.e.*, each interior edge of which is 1 decimetre long. Hence, 1 litre = 1 cubic decimetre = 1000 cubic centimetres. It is equivalent to 1.76 pints or 35.2 fluid ounces.

The Unit of Weight.—The *gram* is the weight of 1 cubic centimetre of distilled water at 4° Centigrade (*i. e.* the temperature of its maximum density). It is equivalent to 15.432 grams nearly. 1 kilogram = 2.2 lbs.

The relation between the weight and volume of water is very simple: the weight being as many grams as the volume is cubic centimetres. Hence, the weight (in grams) of any other liquid = its volume (in cubic centimetres) \times its specific gravity.

Abbreviations are used for the above measures, as *m.* for metre, *l.* for litre, *gr.* for gram, *cm.* for centimetre, *mm.* for millimetre, *c.c.* for cubic centimetre, and so on.

• **Measurement of Volumes of Liquids.**—The following apparatus are used for measuring volumes of liquids:

(1) **Measuring Flask** (Fig. 7).—It is to be filled (at a standard temperature) exactly to the mark etched on the neck. The capacity of the flask is marked on it.

(2) **Measuring Cylinder** (Fig. 8).—It is graduated (the graduations commencing from the bottom), and the numbers 10, 20, 30, &c., are marked against the lines.

(3) **Pipette** (Fig. 9).—It is used for withdrawing and delivering definite volumes of liquids.

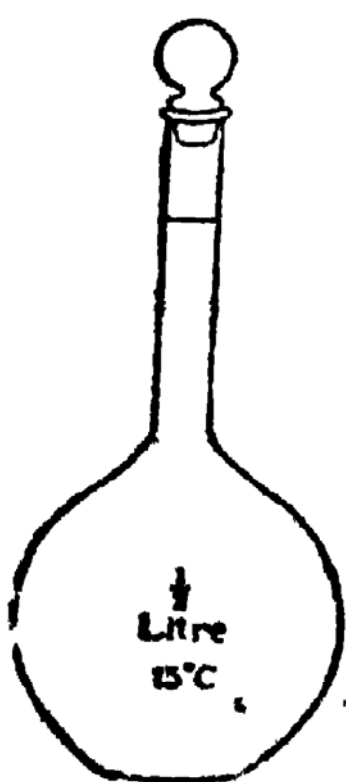


Fig. 7.

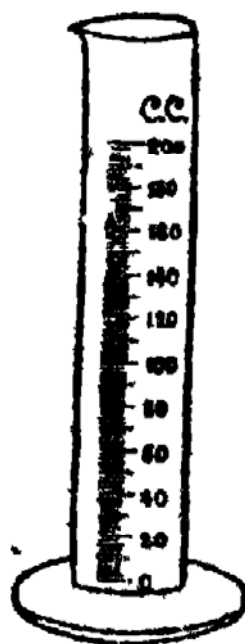


Fig. 8.



Fig. 9.

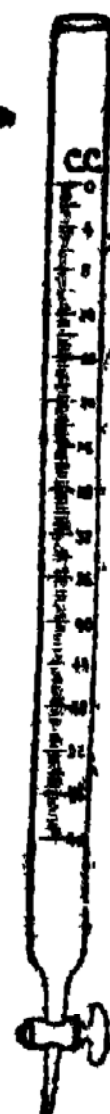


Fig. 10.

The point of the pipette is dipped in a liquid, and by sucking at the other end the liquid is drawn in till its level rises above the mark on the stem: the fore-finger is now quickly placed on the top of the pipette which is then raised up, and by gradually releasing the finger the liquid is allowed to run out till its level reaches the mark.

(4) *Burette* (Fig. 10).—It is a graduated glass tube of uniform bore, open at the top and provided with a tap near the bottom which is drawn to a narrow end. The graduation runs from above downwards, and the instrument is used for *delivering* a definite volume of a liquid. The burette is clamped in a vertical position and then filled in with the liquid which flows out on turning the tap.

NOTE.—The above apparatus are chiefly used when volumes of liquids have to be measured with the greatest accuracy, as in Volumetric Analysis (see Chap. XVI). In using them, specially the burette, the following points should be attended to: (1) At the outset of each operation, the instrument should be thoroughly washed and then rinsed with a little quantity of the liquid to be used. (2) While measuring the volume, notice that the liquid has a curved surface: this curve is called a *meniscus*. Reading should be taken from the lower edge of the meniscus, and the eye of the observer should be level with the meniscus and the graduation. (3) Before delivering the burette, note the graduation at which the liquid stands. It is to be always remembered that the burette (as well as the pipette) does not measure how much it contains, but how much it delivers.

Measurement of Mass: the Balance.—Measurement of mass is usually made with the balance. The *chemical balance* is a very accurate and delicate pair of scales. It is generally made of brass and is enclosed in a glass-case to protect it from dust, draughts, &c.

The chemical balance consists essentially of a beam (AB) having at its ends knife-edges of agate (*a, b*), turned upwards, on which rest the agate planes of the hooks (*c, d*) from which the pans (C, D) are suspended by means of bows *e, f*.

The beam has in the centre another agate knife-edge, turned downwards, resting on an agate plate fixed to the top of the pillar (P). The needle or pointer (*i*), fixed to the centre of the beam and at right angles to it, swings over the graduated scale (S).

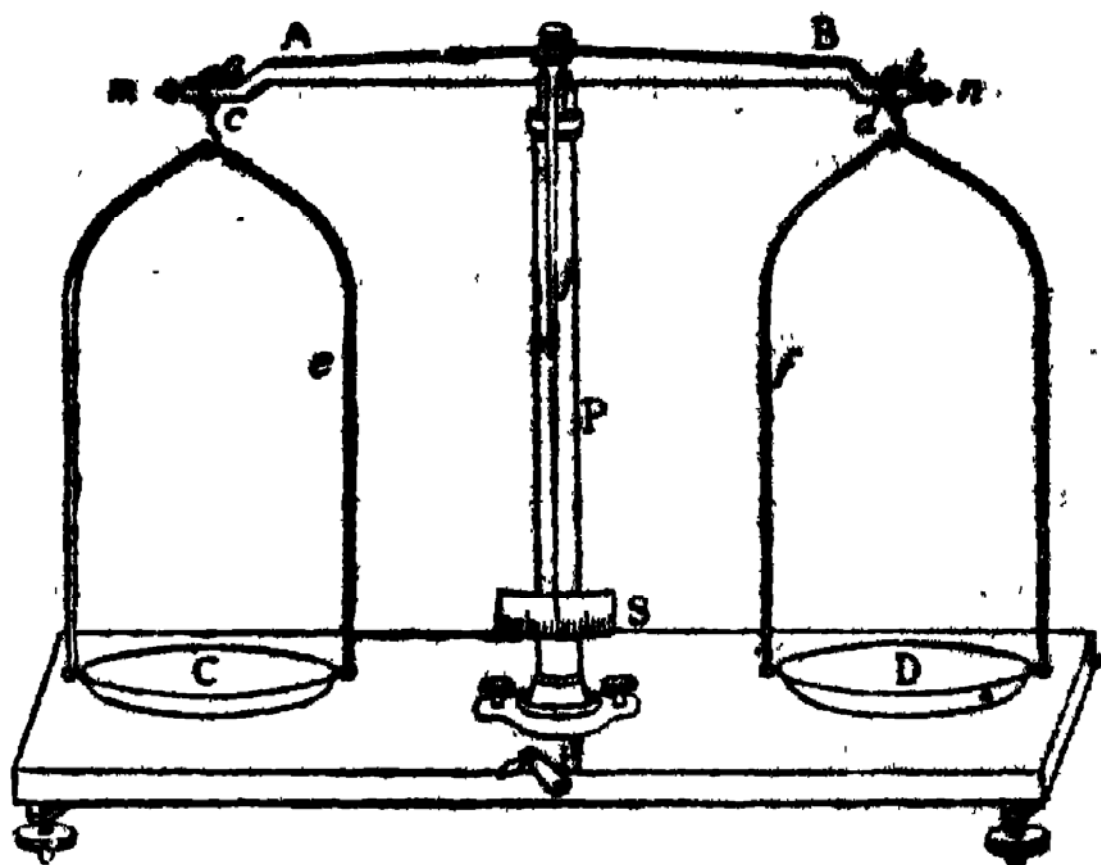


Fig. 11.

When the balance is in adjustment, the pans are free to swing and the pointer moves equally on each side of zero (*i.e.* the central line of the scale). If the vibration be unequal, the adjustment is effected by means of either of the screw-nuts (*m, n*) at the ends of the beam. When the balance is not in use, the handle or screw (*H*) is turned, whereby the agate planes and knife-edges are thrown out of contact and the pans are set at rest.

The Weights.—The set of weights arranged in a box varies with different makes. The weights may range from 500 grams to 1 milligram. A box of weights also contains a pair of forceps for lifting the weights.

Rules to be observed in weighing :—

(1) Before using the balance see that it is in adjustment and that the pans are clean.

(2) Place the object on the left pan and the weights on the right—adding or taking out weights *in order* until the pans exactly balance each other.

(3) Always lift the weights with the forceps, and put the weights back in their respective places.

(4) Do not allow the beam to swing when anything is placed upon or removed from the pans.

(5) Never weigh anything when it is too hot or cold.

(6) Place yourself just opposite the graduated scale, and carefully note the result of each weighing.

Density or Specific Gravity.—The *density* of a body (*i. e.* the quantity of matter contained in a unit volume of it) is estimated by comparing the weight of a given volume of it with the weight of the same volume of a standard substance. In the case of liquids and solids the standard substance is distilled water at $4^{\circ}\text{C}.$, and in the case of gases and vapours it is hydrogen or air at $0^{\circ}\text{C}.$ and 760 mm. pressure. Hydrogen is preferred as the standard, as it is the lightest of all gases.

Hence, the *relative density* or *specific gravity* of a substance is found by dividing the weight of a given volume of it by the weight of an equal volume of water or hydrogen (under standard temperature and pressure). The methods of determining relative densities are given in works on Physics, most of the methods depending on the Principle of Archimedes, that *a body immersed in a liquid loses a part of its weight equal to the weight of the liquid displaced*. The densities of some substances are given below.

Of Liquids and Solids.

Water (at 4°C) 1.00	Sulphur ...	51.9 to 2.05
Bromine 2.96	Graphite 2.20
Mercury 13.60	Glass 2.50
Potassium 0.87	Aluminium 2.60
Sodium 0.97	Diamond 3.50
Magnesium 1.74	Zinc... ..	6.8 to 7.20
Charcoal 1.80	Iron... ..	7.8 to 8.14
Calcium 1.85	Copper 8.95
Phosphorus ...	1.8 and 2.20	Lead 11.40

Of Gases and Vapours.

	Air=1	Hydrogen =1		Air=1	Hydrogen =1
Hydrogen	... 0.069	1.00	Carbon dioxide	... 1.53	22.00
Ammonia	... 0.59	8.52	Sulphur dioxide	... 2.26	32.00
Water	... 0.62	8.90	Chlorine	... 2.48	35.18
Nitrogen	... 0.97	14.00	Bromine	... 5.50	80.00
Air 1.00	14.39	Mercury	... 6.90	100.00
Oxygen	... 1.105	15.88	Sulphur	... 2.20	31.83
Hydrogen sulphide	1.19	17.00	Phosphorus	... 4.28	62.00
Hydrogen chloride	1.26	18.23	Iodine	... 8.80	127.00

Measurement of Temperature: the Thermometer.—

Temperature is measured with an instrument called the *thermometer*. It is a thick glass tube with a fine uniform bore, ending in a spherical or cylindrical bulb filled usually with mercury which rises or sinks in the stem just as the temperature rises or falls. There is a graduated scale usually etched on the stem of the thermometer. The graduations are made on the basis of two definite points: the first is that where the mercury stands when the instrument is plunged into melting ice, the second marks the position to which the mercury rises when the thermometer is surrounded by steam issuing from boiling water. The interval between these two points (*freezing-point* and *boiling-point* of water) is divided in three different ways. (1) In the *Celsius* or *Centigrade* scale the two points are marked 0 and 100, and the interval is divided into 100 spaces called *degrees*. (2) In the *Reaumur* scale the two points are marked 0 and 80 respectively, and the distance is divided into 80 degrees. (3) In the *Fahrenheit* scale the boiling-point is marked 212 and the freezing-point marked 32 (so that there are 180 degrees between them)—the zero point being the temperature of a mixture of sal-ammoniac and snow.

The above scales are indicated by the initial letters C, R, and F respectively. In each scale temperatures are indicated by a small cipher indexed to the particular numbers, and temperatures below zero point are shown by prefixing a minus

sign. Thus, -15°C . means a temperature 15 degrees below zero of the Centigrade scale.

Measurement of Atmospheric Pressure: the Barometer.—The atmosphere or mass of air encircling our globe exerts considerable pressure upon all objects on the surface of the earth. The amount of this pressure is estimated by the following experiment, first performed by Toricelli in 1643. A glass tube, about one yard long and closed at one end, is filled with mercury; with its open end closed with the thumb, the tube is then inverted in a basin containing mercury. The mercury sinks in the tube until (at sea-level) the height of the column is 760 millimetres ($=30$ inches nearly) above the surface of the mercury in the basin. The empty space at the top of the tube is called a *Toricellian vacuum*. The column of mercury in the tube is supported by the pressure of the atmosphere on the mercury in the basin, so that the mercury in the tube rises or falls as the atmospheric pressure varies.

The **ordinary barometer** consists simply of a glass tube about 33 inches long and closed at the upper end, containing mercury and having its lower end dipped into a cup also containing mercury. There is a graduated scale placed along the barometer-tube. The height of the mercury in the tube measures the atmospheric pressure which varies with changes of weather and elevation above sea-level.

CHAPTER III.

PHYSICAL PROPERTIES OF GASES AND VAPOURS.

Relation of the Volume of a Gas to Pressure.—The volume of a given quantity of a gas depends on the pressure to which it is subjected: the volume increases or decreases just as the pressure is decreased or increased. This can be illustrated as follows:

A U-shaped glass tube, with one arm open and 3 feet long and with the other arm closed and nearly 7 inches long, is mounted on a vertical support. Graduated scales are placed against these arms, the zero in both the scales being in the same horizontal line. Mercury is poured into the tube so that it stands at zero in both arms: the air enclosed in the shorter arm is now under the ordinary atmospheric pressure. Mercury is again poured into the tube until the volume of the confined air is reduced to one-half: the difference in the levels of mercury in the two arms is now found to be equal to the height of the barometer. Thus the enclosed air is altogether under a pressure of two atmospheres when its volume is half of what it was under a pressure of one atmosphere.

Boyle's or Mariotte's Law.—Experiments similar to that described above led to the formulation of the law relating to the different volumes of a gas at different pressures. This law of compressibility of gases was discovered first by Boyle and then independently by Mariotte, and is stated thus:—*If the temperature remains the same, the volume of a gas varies inversely as the pressure.* For instance, when the pressure is doubled, the volume of the gas is reduced to one-half; when the pressure is reduced to $\frac{2}{3}$, the gas expands to $\frac{3}{2}$ its original volume.

If V and V' are the volumes occupied by a given quantity of a gas at the pressures P and P' respectively, then according to Boyle's Law, the temperature remaining constant,

$$\bullet \quad \frac{V}{V'} = \frac{P'}{P}; \text{ or } VP = V'P'; \text{ or } V = \frac{V'P'}{P}.$$

NOTE.—As the density of a given quantity of any gas varies inversely as the volume, it follows as a corollary from Boyle's Law that *the density of a gas varies directly as the pressure.*

Boyle's Law is not absolutely true of any gas. Hydrogen, oxygen, nitrogen (and air) obey the law more closely than other gases do. A gas obeying Boyle's Law absolutely would be called a *Perfect Gas*.

Calculation of Volumes of Gases at Different Pressures.—Knowing Boyle's Law we can calculate the volumes

of a certain quantity of any gas at different pressures. It must be remembered that 'normal pressure,' *i. e.* the pressure of the atmosphere at sea-level = the pressure of 760 millimetres (of mercury). See p. 20.

EXAMPLE 1. *If a gas occupies 12 c.c. at 5 atmospheres, to find its volume at 950 mm., the temperature remaining unchanged.*

12 c.c. is the volume at 5 atmospheres, *i. e.* (5×760) mm.

Suppose V is the volume of the gas at 950 mm.

Then, by Boyle's Law, $V \times 950 = 12 \times (5 \times 760)$;

$$\therefore V = \frac{12 \times 5 \times 760}{950} = 48 \text{ c.c.}$$

EXAMPLE 2. *25 c.c. of air at normal pressure is compressed to 19 c.c.; to find the increase of pressure.*

Here suppose P is the total pressure.

$$\text{Then, } P \times 19 = 760 \times 25; \text{ or } P = \frac{760 \times 25}{19} = 1000 \text{ mm.}$$

\therefore The increase of pressure is $(1000 - 760) = 240$ mm.

Relation of the Volume of a Gas to Temperature.—

The volume of a given quantity of any gas depends not only on the pressure it bears, but also on its temperature. That a gas expands when heated and contracts when cooled, may be shown thus :

1. A flask fitted with a rubber stopper through which passes a tube, is inverted so that the tube dips under some coloured water. If we gently heat the flask, bubbles of air will escape—showing that the air in the flask has expanded. On now allowing the flask to cool down, the air will contract and water will rise up the tube to take the place of the air already expelled.

2. Some stout bottles having been filled with different gases are fitted with rubber stoppers through which pass narrow glass tubes bent at right angles. The bottles are then laid in a trough of water so that the tubes point upwards, and a drop of mercury is introduced into each tube. If the water in the trough is now heated uniformly, the mercury will rise equally

in all the tubes—showing that the gases have expanded equally when heated to the same extent. The amount of the expansion is stated in the Law of Charles.

Charles's Law.—The law of expansion of gases, owing to rise of temperature, was discovered by Charles. But the discovery of the law is also attributed to Dalton and to Gay-Lussac. It is thus stated:—*The pressure remaining constant a gas expands by $\frac{1}{273}$ of its volume at $0^{\circ}\text{C}.$ for every degree of rise in temperature.* This constant fraction, $\frac{1}{273}$ or .00366 nearly, is called the *coefficient of expansion*.

Thus, the pressure remaining constant, 1 volume of a gas at $0^{\circ}\text{C}.$ becomes $(1 + \frac{1}{273})$ volumes at $1^{\circ}\text{C}.$; $(1 + \frac{2}{273})$ volumes at $2^{\circ}\text{C}.$; $(1 + \frac{10}{273})$ volumes at $10^{\circ}\text{C}.$; and as a general case

$$\left(1 + \frac{t}{273}\right) \text{ volumes at } t^{\circ}\text{C}.$$

$$\text{Hence, } \frac{\text{volume at } t_1^{\circ}\text{C.}}{\text{volume at } t_2^{\circ}\text{C.}} = \frac{1 + \frac{t_1}{273}}{1 + \frac{t_2}{273}} = \frac{273 + t_1}{273 + t_2}.$$

Absolute Temperature.—The standard temperature is $0^{\circ}\text{C}.$ If, however, the temperature be measured from a point 273° below $0^{\circ}\text{C}.$, we obtain what is called the *absolute temperature*. The absolute temperature is the temperature on the Centigrade scale *plus* 273° . Thus, $0^{\circ}\text{C.} = 273^{\circ}$ Absolute, $15^{\circ}\text{C.} = 288^{\circ}$ Abs., $-15^{\circ}\text{C.} = 258^{\circ}$ Abs., $-273^{\circ}\text{C.} = 0^{\circ}$ Abs.; and generally, $t^{\circ}\text{C.} = (273 + t)^{\circ}$ Abs.

Now, if T and T' be the temperatures on the Absolute scale, corresponding respectively to t_1° and t_2° on the Centigrade scale, then $T = (273 + t_1)$ and $T' = (273 + t_2)$; and if V and V' be the volumes of a gas at these temperatures respectively, then the above formula may be written thus—

$$\frac{V}{V'} = \frac{T}{T'}; \text{ or } VT' = V'T; \text{ or } V = \frac{V'T}{T'}$$

Hence, the Law of Charles is also stated thus:—*The pressure being constant, the volume of a gas is proportional to its absolute temperature.*

Like Boyle's Law, the Law of Charles is only approximately true. Both these laws apply only to gases, not to vapours.

Calculation of Volumes of Gases at Different Temperatures.—Knowing the volume of a gas at a particular temperature, we can (according to Charles's Law) calculate its volume at any other temperature.

EXAMPLE 1. *Two litres of a gas at 0°C. are heated to 100°C.; to find the new volume.*

Suppose V is the volume at 100°C.;

$$\text{then } \frac{V}{2} = \frac{273 + 100}{273 + 0}, \text{ or } V = \frac{2 \times 373}{273} = 2.7 \text{ litres nearly.}$$

EXAMPLE 2. *The pressure remaining the same, 750 c.c. of a gas at 102°C. are cooled down to -90°C.; to find the decrease in volume.*

Suppose V is the new volume (at -90°C.);

$$\text{then, } \frac{V}{750} = \frac{273 - 90}{273 + 102}, \text{ or } V = \frac{750 \times 183}{375} = 366 \text{ c.c.}$$

Hence, the decrease is 384 c.c.

EXAMPLE 3. *To find the temperature at which a given quantity of air will double its volume at 17°C.*

Let x be the required temperature, and V' the volume of air at 17°C.

$$\text{Then, } \frac{2V'}{V'} = \frac{273 + x}{273 + 17}; \therefore 273 + x = 580, \text{ or } x = 307^\circ\text{C.}$$

Calculation of Volumes of Gases at Different Temperatures and Pressures.—It may be required to calculate the volume of a gas when both pressure and temperature vary. In such cases we are first to calculate the volume supposing either the pressure or the temperature to remain constant, and then we are to correct this volume for the alteration of pressure or temperature. Or, we may calculate the volume at once by combining the laws of Boyle and Charles, thus—

From Boyle's Law we have $\frac{V}{V'} = \frac{P'}{P}$; and from Charles's

Law we have $\frac{V}{V'} = \frac{T}{T'}$. Combining these two formulæ we get

$$\frac{V}{V'} = \frac{P'T}{PT'}; \text{ or } V = \frac{V'P'T}{PT'}$$

In calculating the volume of a gas, reference is made to 0°C. and 760 mm. as the 'normal temperature and pressure,' for which *N.T.P.* is frequently used as an abbreviation.

EXAMPLE 1. *A gas occupies 40 c. c. at N.T.P.; to find its volume at 15°C. and 800 mm. pressure.*

N.T.P. means 0°C. and 760 mm. First suppose the pressure remains constant, and calculate the volume at 15°C.—

$$\frac{V}{40} = \frac{273 + 15}{273}, \text{ or } V = \frac{40 \times 288}{273}$$

This being the volume at 760 mm., it is to be corrected for 800 mm.—

$$V \times 800 = \left(\frac{40 \times 288}{273} \right) \times 760$$

$$\text{Or, } V = \frac{40 \times 288 \times 760}{800 \times 273} = 40 \text{ c.c. nearly.}$$

The result may be obtained in one step if we use the combined formula given above.

EXAMPLE 2. *What will 672 c.c. of oxygen at -49°C. and 1100 mm. measure at 357°C. and 1890 mm.?*

Using the combined formula $V = \frac{V'P'T}{PT'}$, we have

$$V = \frac{\text{original vol.} \times \text{original press.} \times \text{new absolute temp.}}{\text{new press.} \times \text{original abs. temp.}}$$

$$= \frac{672 \times 1100 \times (273 + 357)}{1890 \times (273 - 49)} = \frac{672 \times 1100 \times 630}{1890 \times 224} = 1100 \text{ c.c.}$$

Diffusion of Gases.—Diffusion means the spreading of one fluid in another. When a stout bottle containing hydrogen is placed above a stout bottle of oxygen, and the two bottles are held mouth to mouth or are connected by a glass tube, it is found that after a while the two gases mix with each

other. That is, in opposition to gravitation, the light hydrogen gas partly descends into the lower bottle, and the heavier oxygen gas partly makes its way up into the bottle of hydrogen. After some time both the bottles will contain a uniform mixture of the two gases: as may be proved by holding a lighted taper to the mouth of each bottle, when the contents will explode. Similarly it may be proved that other gases interpenetrate and mix with each other. This natural process by which one gas spreads through another, is called *Gaseous Diffusion*. Diffusion goes on both when the gases are placed in contact as well as when they are separated by a thin porous substance (e.g., a layer of plaster of Paris, or a thin earthenware). The lighter the gas, the more readily does it diffuse.

Graham's Law of Gaseous Diffusion.—By performing careful experiments with different gases, Graham discovered that *the rates of diffusion of gases are inversely proportional to the square roots of their densities*. Thus, the densities of hydrogen and oxygen being respectively 1 and 16, their rates of diffusion are as $\sqrt{16}$ to $\sqrt{1}$, that is 4 to 1. In other words, 4 volumes of hydrogen will diffuse in the same time as 1 volume of oxygen.

Atmolysis.—The property of a less dense gas to diffuse more quickly, is made use of in order to separate a gas from a gaseous mixture, and thus to determine the density of a gas and the composition of a gaseous substance. The process of separation of gases by diffusion is called *Atmolysis*. This is illustrated when we pass a mixture of two gases (e.g., hydrogen and oxygen) through a porous material, such as a clay tobacco-pipe. In this case, the light hydrogen will diffuse out through the pipe, and the gas issuing from the other end of the pipe will be found to be chiefly oxygen.

Kinetic Theory of Gases.—Physicists assume that the molecules of a gas are constantly moving rapidly and uniformly in straight lines; and when during this motion they strike against one another or against the walls of the containing vessel, they rebound and continue to move as before in new directions. The pressure

exerted by a gas on the sides of the containing vessel is the combined effect of the 'bombardment' of the vessel by the molecules.

The Kinetic Theory explains the behaviour of gases as stated in the laws of Boyle, Charles, and Graham. (1) When the space occupied by a given mass of a gas is reduced, the number of impacts of the molecules (and so the pressure) on a given area, in a unit of time, is proportionately increased (*Boyle's Law*). (2) When a given quantity of a gas is heated, its pressure increases. This increase of pressure is explained by the Kinetic Theory as due to the increase in the motion (and so of the impacts) of the molecules. If the pressure remained constant, the greater velocity of the molecules would increase the volume of the gas (*Charles's Law*). (3) According to the Kinetic Theory, gases diffuse because their molecules are constantly in a state of motion; the lighter the gas the greater is the velocity of its molecules, and the more rapidly does it diffuse (*Graham's Law*).

[The fact stated in the laws of Boyle and Charles, that different gases behave uniformly when subjected to the same alteration of pressure and temperature, can be explained on the supposition that 'equal volumes of all gases contain the same number of molecules' or that 'the molecules of all gases occupy the same space.' This hypothesis is what is known as *Avogadro's Law*].

Liquefaction of Gases.—Under special conditions of temperature and pressure all gases can be liquefied. When gases are thus condensed they do not, of course, follow the laws of Boyle and Charles. By applying cold and pressure, Faraday liquefied such gases as chlorine, ammonia, hydrogen chloride, sulphur dioxide. But hydrogen, nitrogen, oxygen, carbon monoxide, and a few other gases could not be liquefied by Faraday by the means at his disposal; and accordingly these gases came to be regarded as the *permanent gases*. Subsequently however, Pictet and Cailletet liquefied oxygen by subjecting it to great cold and pressure. Wroblewski condensed nitrogen and carbon monoxide, and so late as in 1898 Dewar obtained liquid hydrogen.

Critical Temperature and Pressure.—Andrews discovered (in 1869) that when the temperature of carbon dioxide was above

32°C., no amount of pressure was able to liquefy the gas; the gas could only be liquefied when its temperature was below 32°. So it has been found that for every gas there is a certain temperature, above which it is impossible to effect the liquefaction of the gas. This particular temperature for a gas is called its *critical temperature*, and the pressure required to liquefy a gas at its critical temperature is known as its *critical pressure*. The critical temperatures and pressures of hydrogen, nitrogen and oxygen are the following—

Hydrogen	...	—240°C. nearly	...	15 atmospheres nearly
Nitrogen	...	—146°C. „	...	35 „ „
Oxygen	...	—119°C. „	...	50 „ „

Vapour and Vapour Pressure.—A *Vapour* is the gaseous form of a substance that is ordinarily a liquid or a solid. It is thus distinguished from a true gas which at ordinary conditions of temperature and pressure remains in the aeriform state. “A *vapour* is a gas whose critical temperature is within the range of ordinary terrestrial temperatures. A ‘permanent’ gas is one which, at ordinary temperatures, is not condensable into liquid by pressure only.”

Evaporation is the slow formation of vapour on the surface of liquids. It goes on at all temperatures; but the higher the temperature of the liquid the more rapidly does it evaporate.

Vapour Pressure.—The vapour of a liquid exerts pressure. With the rise of temperature, more liquid is evaporated and so the pressure increases. The quantity of vapour that can be formed within an enclosed space is however limited. When a close space contains as much vapour as it can contain at a particular temperature, the space is said to be ‘saturated’ with the vapour. In such a case the vapour exerts its highest pressure, tension, or elastic force. The pressure exerted by the saturated vapour of a liquid at a particular temperature is called its *vapour tension* or *vapour pressure*.

At the same temperature, vapours of different liquids have different pressures. In other words, *vapour pressure depends*

on the temperature and on the nature of the liquid evaporated. This may be experimentally proved as follows.

Four tubes, about 3 feet in length and closed at one end, are completely filled with mercury and inverted over a mercury trough. One of the tubes serves as a barometer; and a few drops of water, alcohol, and ether are introduced (by means of a syringe or pipette) into the second, third, and fourth tubes respectively. As soon as the liquids reach the vacuum in the tubes, they are changed into vapour, and the vapours depress the mercury in the tubes to different extents. Thus, at $20^{\circ}\text{C}.$, the vapour of water depresses the mercury nearly 17 mm., alcohol vapour depresses it nearly 3 times as much, and ether vapour 25 times as much. The extent of depression in each tube represents the vapour pressure of the particular liquid for the temperature at which the experiment is made.

Relation of Vapour Pressure to Boiling-point.—If, in the above experiment, the tube in which water has been introduced is surrounded by a wider tube through which steam from boiling water is passed, the water in the tube gradually attains the temperature of the steam surrounding it, and the mercury in the tube is more and more depressed until it reaches the level of the mercury in the trough. The pressure of water vapour in the tube is in this case equal to the atmospheric pressure on the mercury. Similarly, when the third and fourth tubes are surrounded by the vapour of boiling alcohol and ether respectively it is found that the mercury in the tubes is depressed to the level of that in the trough. Hence we conclude that the vapour pressure of a liquid at its boiling temperature is equal to the atmospheric pressure. In other words, *the boiling-point of a liquid is that temperature at which its vapour pressure is equal to the atmospheric pressure on the liquid.* Thus the boiling-point of a liquid is raised or lowered according as the pressure is increased or decreased.

University Examination Questions.

1. Explain Boyle's Law [C. 08].

2. State Charles' Law [A. 04].

60 cubic inches of hydrogen, originally measured at 20°C ., are cooled to -20°C . What will now be the volume of the gas ? [A.04]

3. State the relation between the volume, pressure and temperature of a given quantity of a gas [C. 99 ; A. 02]. Explain clearly the influence of pressure and of temperature on the volumes of gases. How would you proceed practically to show the effect of a change of temperature on the volume of a gas ? [C. 1913].

4. What do you understand, by the terms 'normal pressure' and 'normal temperature' ? Why is it necessary to compare the volumes of gases at the same temperature and the same pressure ? [C. 03]. Why is it necessary to know the temperature of a gas, and to read the height of the barometer, when determining gas volumes ? [A. 03].

5. When the pressure is 760 mm. and the temperature 0°C ., the volume of a gas is 910 c. c. What will be the volume of the same gas when the pressure is 728 mm. and the temperature is 27°C ? [C. 99].

When the pressure is 735 mm. and the temperature 27°C ., the volume of a gas is 2895 c.c. What will be the volume of the same gas in litres at N. T. P. ? [A. 02].

A volume of hydrogen measures 1 cubic decimetre at 20°C . under a pressure of half an atmosphere. How many c.cs. will it occupy at 10°C . and 700 mm. pressure ? [A. 03].

6. Write a short note on Gaseous Diffusion [A. 1915]. 'State the law which regulates the diffusion of gases [A. 05].

How does the kinetic theory of gases account for the different rates of diffusion of different gases ? [A. 1911].

7. What do you mean by 'atmospheric pressure' ? How can it be measured ? State also what is meant by 'vapour pressure' and describe an experiment which proves that at a given temperature different substances have different vapour pressures. [A. 01]

● CHAPTER IV.

ORDINARY CHEMICAL OPERATIONS.

Common Methods of Separation.—The following are the ordinary laboratory methods for separating and purifying substances, viz., Solution, Decantation, Filtration, Evaporation, Distillation, Sublimation, Crystallization, Desiccation, and Ignition.

(1) **Solution.**—It is the process of dissolving substances in liquids. The liquid which dissolves a thing is called the *solvent*, while the substance itself is said to be soluble in the particular liquid. By solution we can separate a soluble substance from its mixture with insoluble substances. When we have got, for example, a mixture of sand and sugar, we may separate the sand by adding water to the mixture; the sugar will be dissolved and the sand will settle down. When we have dissolved as much of a substance (whether a solid or a gas) as can possibly be dissolved in a certain quantity of a liquid, the solution is said to be *saturated*.

(2) **Decantation.**—It means carefully pouring a liquid without disturbing the sediment over which the liquid stands. By this means we obtain a clear liquid free from solid particles.

(3) **Filtration.**—This consists in passing a liquid through a porous substance which retains the solid matter that was mixed up with the liquid. Thus, when a mixture of chalk and water is poured over filter-paper, the chalk is retained on the paper and the water passes through. The liquid obtained by filtration is called the *filtrate*. By filtration a liquid is freed from the solid particles held *in suspension* (i. e. floating in the liquid).

(4) **Evaporation.**—It means the conversion of a liquid into vapour by the application of heat. By this process we

recover a solid held in solution in a liquid. Thus, by heating a solution of sugar, the water passes off as steam and the solid sugar remains behind.

(5) **Distillation.**—This consists in the combination of the opposite processes of Evaporation and Condensation. The liquid to be distilled is first converted into vapour which is then condensed in a cool vessel. By this means a liquid is freed from non-volatile impurities contained in it. The liquid obtained after distillation is called the *distillate*.

Leibig's Condenser (Fig. 12).—This is an apparatus conveniently used for distillation. It consists of a glass tube C fitting inside another tube D; the tube C is kept cool by a current of cold water entering the tube D through *d* and passing out through *e*. The liquid to be distilled is heated in the flask A: after it has commenced to boil, its vapour passes through the tube

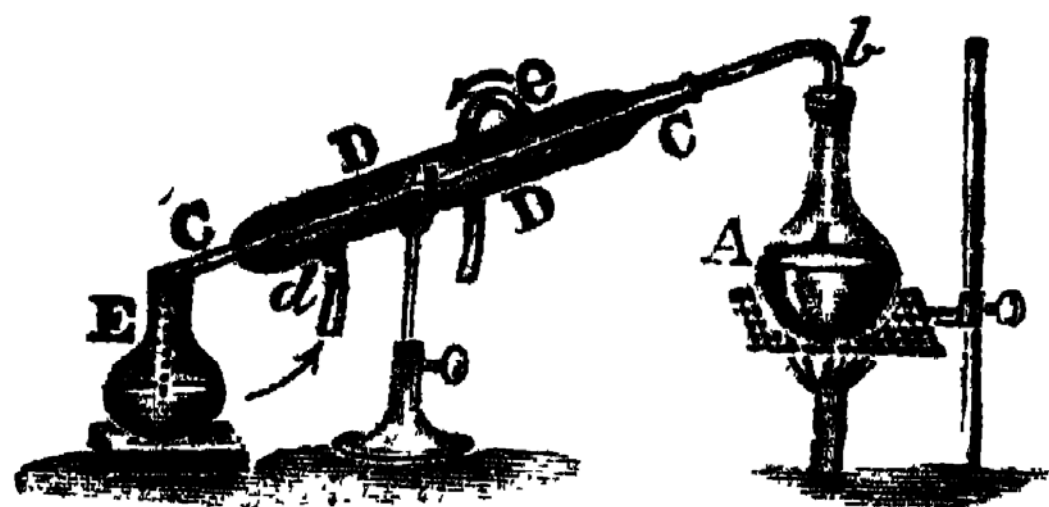


Fig. 12.

b into the condenser, and all solid matter that was mixed up with the liquid remains behind in the flask. The vapour, on entering the cold tube C, is condensed

to a liquid which trickles down and is collected in the receiver E.

Fractional Distillation.—This is the method employed when we have to separate two or more liquids that have widely different boiling-points. A mixture of the liquids being heated, they vaporize in the order of their volatility; and when the distillates are successively collected in separate vessels, the earlier distillates contain more of the low-boiling liquids, while the later distillates contain more of the high-boiling ones. These fractional distillates being repeatedly distilled, a more or less complete separation of the liquids is effected. This process of distilling liquids in portions is called *Fractional Distillation*.

For instance, when we have to separate alcohol from water, we heat the mixture of the liquids and separately collect the distillates at about 78°C . and 100°C . (the respective boiling-points of alcohol and water). The distillates being redistilled in the same way, and by repeating the process if necessary, we obtain nearly pure alcohol and pure water.

Dry or Destructive Distillation.—This process (used in the manufacture of coal-gas from coal, charcoal from wood, and so forth) consists in heating a substance in a closed vessel, so that air cannot enter and the substance cannot burn up : by this means the volatile products (*e. g.* gas and tar) pass off, and the solids (*e. g.* coke, charcoal) remain behind.

(6) **Sublimation.**—It is the process of converting a solid into vapour and then reconvertng the vapour into the solid. If we heat in a vessel some camphor or sal-ammoniac, the substance will not melt into a liquid but will pass off into vapour which will condense as crystals on the upper part of the vessel ; nothing will be left in the vessel excepting some impurities with which the substance might have been mixed up. The solid obtained by sublimation is called the *sublimate*.

Substances which pass off as vapour, and can therefore be distilled or sublimed, are called *volatile*. Those which cannot be distilled or sublimed are called *fixed*.

(7) **Crystallization.**—It is the method of obtaining solid substances in the shape of crystals. Crystals may be formed in the processes of Distillation and Sublimation ; they are also obtained by cooling a fused mass (as in the preparation of prismatic sulphur), or by evaporating the solution of a solid (as when crystals of sulphur are obtained from its solution in carbon disulphide). By crystallization we purify solids and separate less soluble solids from more soluble ones.

(8) **Desiccation or Drying.**—It is the process of removing moisture (*i.e.*, traces of water) from gases. Quicklime, sulphuric acid, calcium chloride, phosphorus pentoxide, &c. are very good desiccating agents ; hence a gas is dried by

passing it (according to the nature of the case) through one of these substances which absorb all moisture.

(9) Ignition.—It means strongly heating or setting fire to a substance. When one thing has to be separated from another which can be burnt, we take advantage of the situation by strongly heating the mixture so that the latter component may burn off.

Collection of Gases.—For experimental purposes gases are collected in gas-jars or bottles. The tube by which the gas passes from the generating apparatus to the gas-jar, is called the *delivery tube* or *leading tube*. The method of arrangement of the delivery tube and the gas-jar varies according to the nature of the particular gas to be collected—

I. When the gas is insoluble or is only slightly soluble in water, it is collected over the pneumatic trough, i. e. by displacement of water. The following is the method:—Pour water into the trough so as to cover the shelf; fill the gas-jar completely with water, and, having closed its mouth with the plate, invert and place it with its mouth under the water in the trough; now remove the plate. The generating apparatus being ready, place the free end of the delivery tube under the shelf in the trough. When the gas has driven all the air from the apparatus, place the gas-jar over the shelf, taking care that the mouth of the jar is always under the surface of the water. When the

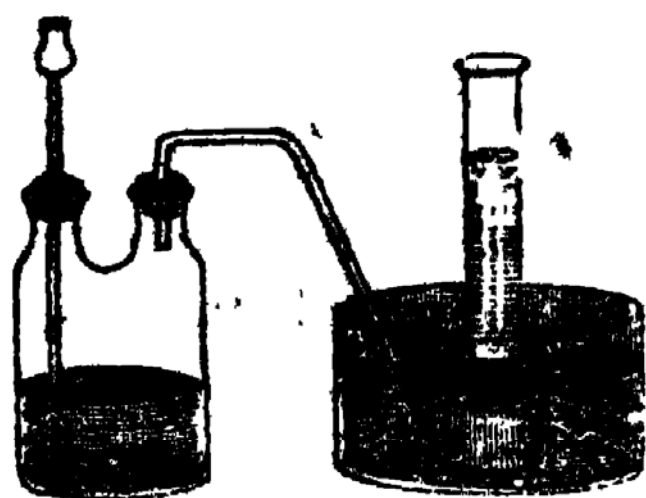


Fig. 13.

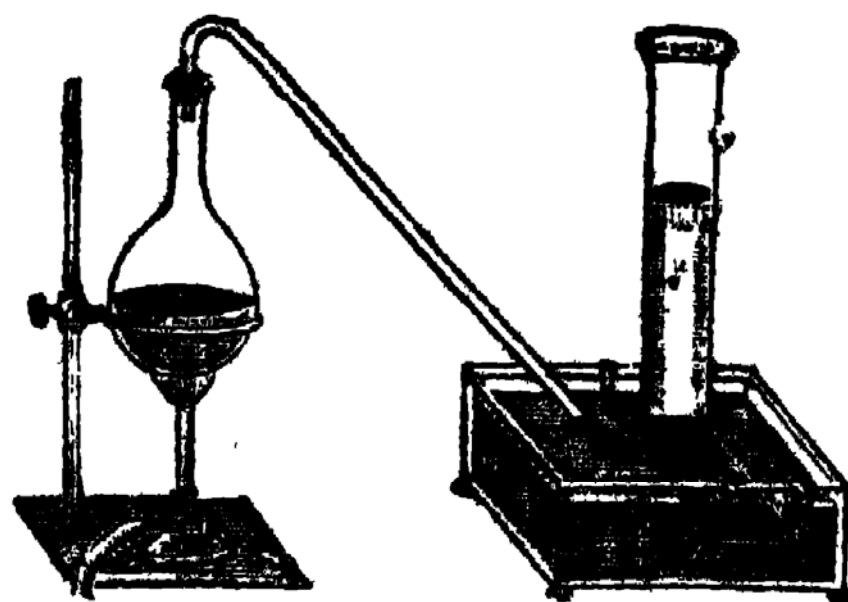


Fig. 14.

jar is filled with the gas, close its mouth with the plate, and remove it from the trough.

The following gases are collected by this method—

- (i) Hydrogen, nitric oxide, carbon dioxide, acetylene, sulphuretted hydrogen ;
- (ii) Oxygen, nitrous oxide, carbon monoxide, marsh gas, ethylene.

The first five are prepared without heat (Fig. 13); the last five require the application of heat in their preparation (Fig. 14).

II. When the gas is soluble in water and is heavier than air, it is collected by downward displacement of air. For this purpose the gas-jar or bottle is placed upright (i. e. mouth upward) and its mouth is loosely covered with ordinary paper or cardboard. The delivery tube is led into the jar, after being passed through one or more wash-bottles where the gas is purified. (Fig. 15).

Chlorine, hydrochloric acid, and sulphur dioxide are collected by this method. All these gases are prepared by the application of heat.

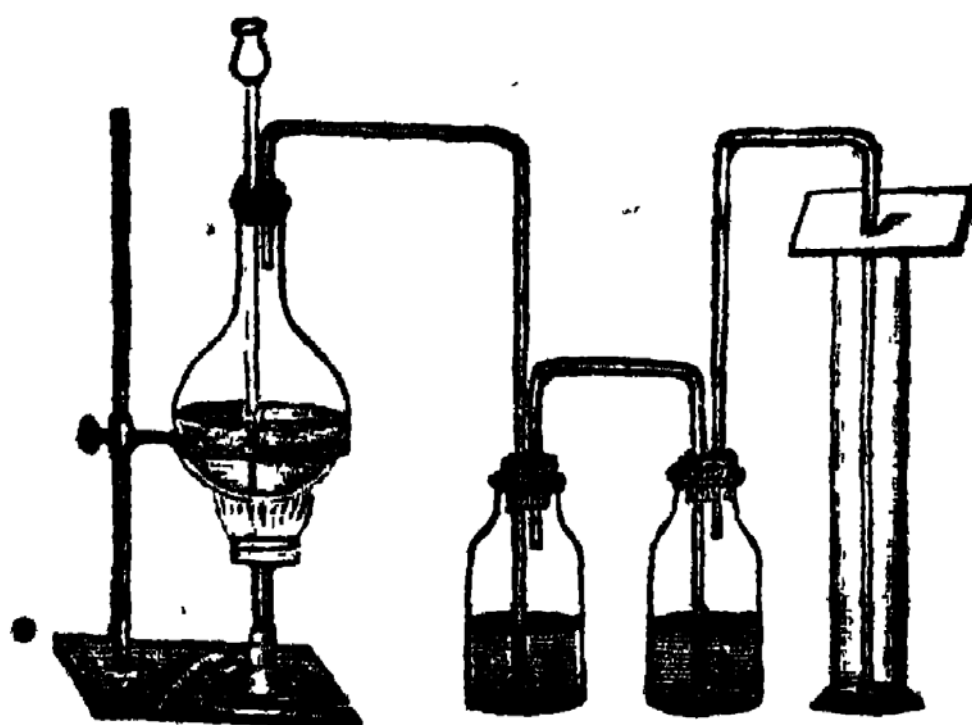


Fig. 15.

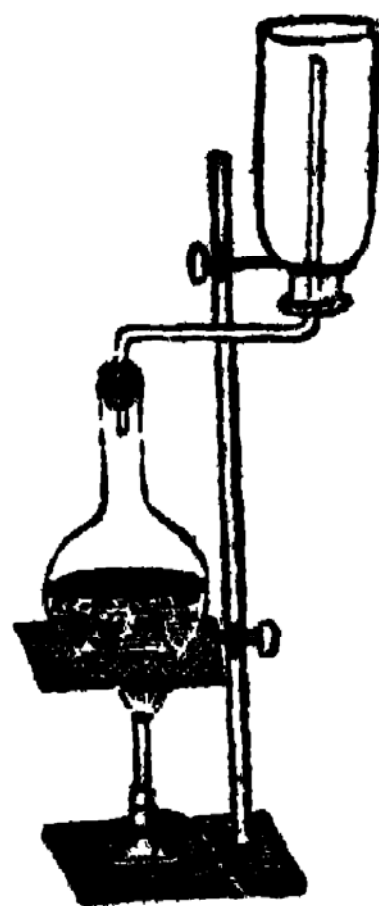


Fig. 16.

III. When the gas is soluble in water and is lighter than air, it is collected by upward displacement of air. In this arrangement the delivery tube is led upright, and the gas-bottle is held inverted over it. (Fig. 16). Ammonia is collected by this method.

University Examination Questions.

1. Explain the meaning of the terms Destructive Distillation and Distillation [C. 93] Describe the process known as *distillation*. Wherein does it differ from 'destructive distillation'? [A. 94].
2. Explain the term Crystallization [C. 1910], Sublimation [C. 1911]. Illustrate by examples.

CHAPTER V.

SOLUTION AND CRYSTALLISATION.

Solutions.—A solution is the homogenous mixture of a substance with a liquid. We may have the solution of a gas with a liquid, of a liquid with another liquid, or of a solid with a liquid. The liquid which dissolves a substance is called a *solvent*. When a gas is dissolved in a liquid, the liquid is said to *absorb* the gas. Water is the most common of all solvents; other solvents are alcohol, ether, turpentine, &c.

Solution of Gases.—Nearly all gases are more or less soluble. The solubility of a gas depends on the nature of the gas and of the solvent, the temperature of the solvent, and the pressure of the gas. *Gases are less soluble in hot liquids than in cold*; hence, when a solution of a gas is heated, some of the dissolved gas is expelled.

Henry's Law.—Henry discovered that the quantity (*i.e.*, mass) of a gas absorbed by a liquid is proportional to the pressure. But as the volume of a given quantity of a gas is inversely proportional to the pressure (Boyle's Law), Henry's Law is stated thus:—*A given volume of a liquid absorbs the same volume of a gas at all pressures.* Thus, if a quantity of water absorbs x grams of oxygen under a pressure of one atmosphere, it will absorb $2x$ grams of oxygen under a pressure of two atmospheres. But as, by Boyle's Law, x grams under a pressure of 1 atmosphere occupy the same volume as $2x$ grams under a pressure of 2 atmospheres, the *volume* of the

gas dissolved by the given quantity of the liquid remains the same at both the pressures. Henry's Law finds practical application in the manufacture of aerated waters.

Coefficient of Solubility.—The solubility of a gas in a particular liquid, called the "coefficient of solubility or absorption," is determined by the volume of the gas that can be absorbed by a unit volume of the liquid at 0°C . and 760 mm. pressure.

Solubility of a Mixture of Gases: Law of Partial Pressures.—Dalton discovered that the pressure of a mixture of gases is the sum of the pressures which they would exert independently: the pressure of each of the component gases is thus called its *partial pressure*. It follows therefore from Henry's Law that when a mixture of two or more gases is in contact with a solvent (with which the gases do not act chemically), *the solubility of each gas is proportional to its partial pressure*. This is known as Dalton's Law of Partial Pressures.

The solution of air in water illustrates this law. As air contains by volume $\frac{1}{5}$ oxygen and $\frac{4}{5}$ nitrogen, the partial pressures of the gases are $\frac{1}{5}$ and $\frac{4}{5}$ of an atmosphere. Taking the coefficients of absorption of the gases as .04 and .02, the amounts dissolving in 1 volume of water are $.04 \times \frac{1}{5} = .008$ and $.02 \times \frac{4}{5} = .016$ respectively. That is, 100 volumes of water dissolve .8 volume of oxygen and 1.6 volumes of nitrogen—altogether 2.4 volumes of air.

Solution of Liquids.—Of liquids which form a homogeneous mixture with each other, some are miscible in any proportions, while others mix only slightly and in definite quantities. For example, water can be mixed with alcohol in any proportion, but not so with ether.

Liquid Diffusion.—When liquids which can mix with each other are placed in layers, one above the other (the lighter being at the top), they are found after some time to have formed a homogeneous mixture. This spreading of one liquid into another resembles the diffusion of gases, and is called *Liquid*

Diffusion. It appears, therefore, that though a liquid may seem to remain quite motionless, its particles are in a state of motion. Liquid diffusion goes on even when the liquids are separated by a membrane (such as, bladder or parchment-paper); the diffusion of liquids through such a membrane is called *Osmose*.

Solution of Solids.—Of solids, some are soluble in water, some are only imperfectly soluble, and others are insoluble. Some solids do not dissolve in one liquid, but are soluble in other liquids. For example, shellac is dissolved by alcohol but not by water, sulphur is soluble in carbon disulphide but not in water or alcohol, bees-wax can be dissolved by oil of turpentine alone.

The solubility of a solid generally increases with rise of temperature of the solvent: that is to say, the higher the temperature of the liquid the greater is its power of dissolving a solid. Common salt is, however, almost equally soluble in hot and cold water. The solubility of a solid at a particular temperature is defined as the number of grams of the solid dissolved by 100 grams of water at that temperature. [For a Table of Solubilities see Appendix].

Saturated Solution.—When a liquid has dissolved at a particular temperature as much of a solid as it can, the solution is said to be *saturated*. A saturated solution at a given temperature may be prepared in two ways:—(1) by maintaining the liquid at the particular temperature, and gradually dissolving in it more and more of the solid by constant stirring or shaking; or (2) by dissolving in the liquid at a higher temperature an excess of the solid, and then cooling the solution to the required temperature, after adding to it a fragment of the solid.

In the latter method a fresh fragment of the solid is added in order that the excess amount of dissolved solid may be readily deposited. Unless this be done, the solution may cool down without parting with the excess of the solid dissolved: the solution in this case being called *supersaturated*.

Separation of Solids from a Mixture.—When a mixture contains solids, one of which is soluble and another insoluble in a particular liquid, we may separate the solids by means of that liquid. We may thus also ascertain the respective amounts of the soluble and insoluble parts of a mixture.

Separation of the components of Gunpowder.—Gunpowder is a mixture of nitre, sulphur, and charcoal. Of these, nitre is dissolved by water, and sulphur by carbon disulphide, while charcoal is not soluble in either of these liquids.

Let us put a quantity of the gunpowder in a beaker, pour warm water over it, shake, and then filter. A moist mixture of sulphur and charcoal will be left on the filter-paper, while the filtrate will contain the nitre. If we now dry the residual mixture, treat it with carbon disulphide, and then filter, charcoal alone will be left on the filter-paper. On evaporating the two filtrates we obtain the nitre and the sulphur.

Determining the Percentage of the Soluble and Insoluble Parts of a Mixture.—We put a weighed quantity of the mixture in a porcelain dish, pour into it water or the suitable solvent, stir for some time, and (when the undissolved portion has settled down) pour the liquid through a weighed filter-paper. We add again a little of the solvent, stir, and filter the liquid through the paper. When all the soluble portion has been filtered off, we transfer the insoluble substance to the filter-paper, and wash it thoroughly with the solvent. Now we dry the insoluble matter and the paper, and weigh.

The percentage of the substances may be calculated as in the following example—

Weight of mixture	4	grams
„ „ filter-paper	0.5	„
„ „ filter-paper and insoluble part	2.73	„
„ „ insoluble part	$(2.73 - 0.5) =$		2.23	„

Thus, 4 parts of the mixture contain 2.23 parts of insoluble matter. We have to calculate what will 100 parts of the mixture contain :

$$4 : 100 :: 2.23 : x. \quad \therefore x = \frac{100 \times 2.23}{4} = 58.5 \text{ parts Insoluble.}$$

$$\therefore 100 - 58.5 = 41.5 \text{ „ Soluble.}$$

Finding the Solubility of a Solid.—To find the solubility of a solid at a certain temperature, we take a flask containing some water and place it in a water-bath kept constantly at the particular temperature. We gradually add the powdered solid to the water in the flask, and shake well, until a portion of the solid remains undissolved. After the undissolved solid has settled down, we transfer a little of the solution to a previously weighed porcelain dish, and weigh when the solution is cool. We then evaporate and dry the contents of the dish, and weigh them when cool.

The results are calculated in the following way—

Second weighing ... 28.73 grams = weight of dish and solution

First „ ... 20.56 „ = „ „ dish

Difference ... 8.17 „ = „ „ solution

Third weighing ... 21.98 grams = weight of dish and solid.

First „ ... 20.56 „ = „ „ dish

Difference ... 1.42 „ = „ „ solid

That is, (8.17 — 1.42) grams of water dissolve 1.42 grams of solid

\therefore 100 „ „ „ „ x „ „ „

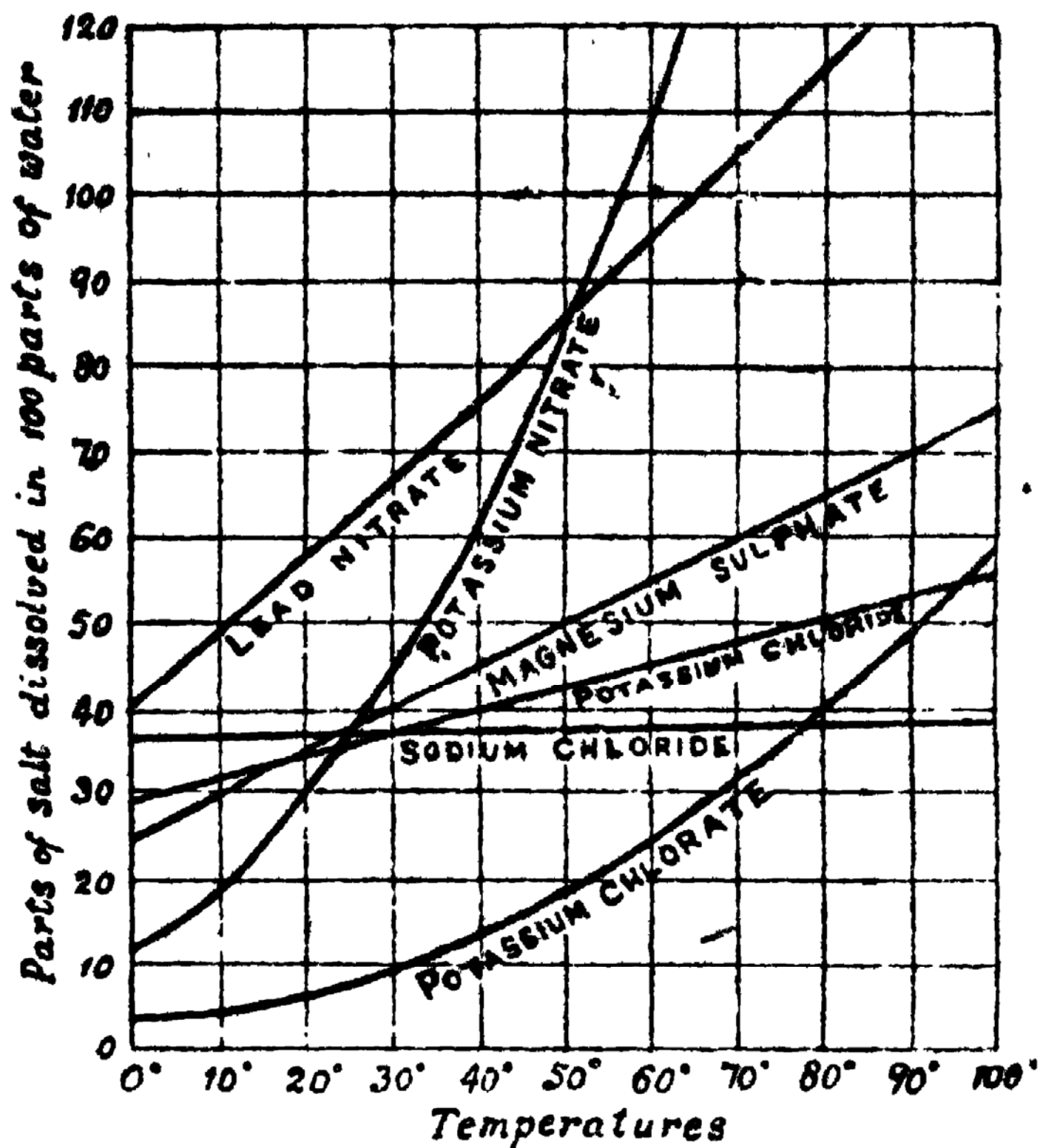
$$\text{where } x = \frac{100 \times 1.42}{6.75} = 21 \text{ grams.}$$

Solubility Curves.—The solubility of various salts at different temperatures are graphically represented by means of curves (Fig. 17). The vertical lines indicate temperatures, and the horizontal lines indicate the number of parts of a salt that can be dissolved by 100 parts of water. Thus, 100 grams of water dissolve 30 grams of potassium nitrate at 20°C., 62 grams of it at 40°C., and so on. Common salt (sodium chloride) is soluble in water almost equally at all temperatures.

Crystals.—Crystals are homogeneous solids which have definite geometrical forms and which reflect light from their

plane faces. Solids that are not crystalline are called *amorphous*. Crystalline solids can be distinguished from amorphous

Fig. 17.



bodies when they are broken : an amorphous substance shows irregular structure and breaks in any direction, while a crystal splits in definite directions (called *cleavage*) and its fragments have regular shapes.

Crystals are classified in six groups or systems, *viz.* (1) Cubic or Regular, (2) Quadratic or Pyramidal, (3) Trimetric or Rhombic, (4) Monoclinic, (5) Triclinic, and (6) Hexagonal. The same substance usually crystallises in the same form. But there are some substances (as carbon, sulphur) which may assume two distinct crystalline shapes : such things are called *dimorphous*. Sometimes different compounds crystallise in the same form : these are said to be *isomorphous* with each other.

Isomorphism.—It means similarity of form. Substances having similar chemical constitution often crystallise in the same form. Thus, zinc sulphate forms crystals of the same geometrical form as ferrous sulphate or magnesium sulphate. So the crystals of ammonium chloride and potassium chloride are found to be similar. Such pairs of compounds are accordingly called *isomorphous*. There are two characteristics of isomorphous substances :—(1) They form *layer crystals*, i.e., when a crystal of one such substance is placed in a solution of another, it continues to grow without change of form—a layer of the second substance being deposited on the crystal. (2) They form *mixed crystals*, i.e., when a solution containing two such substances is allowed to crystallise, we get homogeneous crystals of a mixture of the two substances.

[The phenomenon of isomorphism is sometimes made use of as a confirmatory test in determining the atomic weights of elements. For instance, in the case of a crystal of zinc sulphate, magnesium may be replaced for zinc without altering the crystalline form of the substance. The replacement is here *atom for atom*. Knowing the atomic weight of zinc to be 65, if the weight of magnesium required to replace this weight of zinc is found to be 24, this number is taken as the atomic weight of magnesium.]

Formation of Crystals.—Crystals are formed in one of three ways :—(1) by the cooling or evaporation of a saturated solution of a solid, as when crystals of copper sulphate are obtained from their solution in water; (2) by the solidification of a fused substance, as when prismatic sulphur is obtained by melting ordinary sulphur; (3) by the condensation of vapours of volatile solids, as when camphor or iodine is obtained by sublimation.

The more slowly do crystals grow, the bigger and more regular are they in size and structure.

Water of Crystallisation.—Many crystalline salts enter into a feeble chemical union with water : and when the water

contained in them is removed the crystalline form of the substances is destroyed. Water thus associated with crystals as an essential part of their constitution, is called *water of crystallisation*. Thus, crystals of copper sulphate contain about 36 per cent. of water. Other examples of crystals containing water are crystals of washing-soda, gypsum, common alum.

Water of crystallisation can be driven off by heat. Thus, when we heat crystals of copper sulphate, water is evolved, the crystals lose their blue colour and are reduced to a white powder. If now some water is added to the powder, heat is generated, and the blue crystals are again formed.

Substances containing water of crystallisation are called *hydrated*, as distinguished from substances which contain no water and which are therefore called *anhydrous*. Thus, the blue crystals of copper sulphate are hydrated; but when the substance is reduced to a white powder by heating, it is anhydrous. It is to be noted that water is not an essential part of all crystals; for example, crystals of common salt and of potassium chlorate are anhydrous:

Efflorescence and Deliquescence.—Certain substances containing water of crystallisation slowly part with it when they are exposed to the air: such crystals are called *efflorescent*, and this process of losing water of crystallisation is called *efflorescence*. For example we have sodium carbonate (or washing-soda) which when exposed to the air for some time is reduced to a powdery mass. On the other hand, *deliquescence* is the property which certain solids have of absorbing moisture from the air and of becoming moist and sometimes liquid: these bodies are called *deliquescent*. Calcium chloride and potassium carbonate are examples.

Determination of Water of Crystallisation.—The percentage of the water of crystallisation of a solid (*i.e.* the amount of water of crystallisation contained in 100 grams of a hydrated solid) can be determined in the following way:

We weigh a porcelain crucible, put in it a gram or two of

the crystals, and weigh again. The substance is then gently heated for some time. When the substance is perfectly dry we remove the crucible, allow it to cool in a desiccator, and weigh again.

The results are then calculated thus—

Second weighing...16.57 grams = weight of crucible + crystals

First " ...15.07 " = " " crucible

Difference... 1.5 " = " " crystals

Second weighing...16.57 grams = wt. of crucible + crystals

Third " ...15.63 " = " " crucible + (crystals—water)

Difference... 0.94 " = " " water

That is, 1.5 grams of crystals contain 0.94 gram of water

∴ 100 " " " " x " " "

when $x = \frac{100 \times 0.94}{1.5} = 62.7$ grams nearly.

Hence, the composition of the crystals is approximately this :—anhydrous solid 37.3 per cent., and water 62.7 per cent.

University Examination Questions.

1. What is meant by 'saturated solution' [C. 08], 'solubility' of a salt? [C.03].

2. Explain the influence of temperature on the solubility of (a) a solid, and (b) a gas in water [C.08].

3. If a mixture of nitre or salpetre and sand is given to you, how can you obtain from the mixture, solid nitre free from sand? [C.03]. You are given a mixture of sand, chalk, and common salt. Describe how you can find out the percentage of the three constituents in the mixture, explaining clearly the various operations involved [C.1910]. How would you separate the constituents of a sample of gunpowder? [C.1915].

4. Give a clear account of the method you would use to determine the solubility of common salt at the temperature of the air [C.05].

5. Explain the use of solubility curves [C.05]. Show by a curve the difference in the solubility of potassium nitrate and sodium chloride in 100 parts of water between 0°C. and 60°C. [C.08].

6. Explain the following terms :—crystal [C.03], isomorphism

[C 1915, 16], water of crystallization [C. 07, 1911, 14], deliquescence [C. 03, 99, 07, 1910 ; A. 1914], efflorescence [C. 07, 1911, 16].

7. Describe fully how you would proceed to determine the water of crystallization of copper sulphate, and give its formula before and after the operation [C. 1911, 14].

8. What are crystals, and how are they generally prepared? How would you prepare crystals of sulphur, saltpetre, and green vitriol? What would happen if you heat these crystals? [C. 1916].

CHAPTER VI.

COMBUSTION AND THE FLAME : OXIDATION AND REDUCTION.

Combustion.—*Combustion is chemical union of two substances attended with heat and light.* Ordinarily it means chemical union of a substance with the oxygen of the air, such union being accompanied with evolution of heat and light. Combustion may be (1) *active* or *rapid*, when it is called *burning*, or (2) it may be *slow*, as when iron gradually rusts in the air, or when moist organic substances undergo *decay* by being exposed to the air. In the latter case the production of heat is not apparent.

Ignition and Incandescence.—Ignition means heating very strongly, and seems to include combustion as well as incandescence. In the case of combustion a substance is changed materially, as is the effect of igniting coal or magnesium. In the case of incandescence, on the other hand, a substance glows with light, becoming first red-hot and then white-hot, without undergoing any chemical change ; such is the case when quick-lime or platinum is ignited, or when the carbon filament glows in the vacuum of an 'incandescent lamp.'

Combustible Bodies and Supporters of Combustion.—Ordinarily, in cases of combustion, the substance which burns (*e.g.*, hydrogen, coal-gas) is called the *combustible* or *inflammable body*, and the air or oxygen which surrounds the burning

substance is called the *supporter of combustion*. What actually takes place in these cases, however, is chemical union of oxygen with the inflammable body; and the combustion would equally take place if the order of these substances were reversed. Thus, a jet of air or oxygen burns as freely in hydrogen or coalgas, as the latter burns in the former. *The terms combustible and supporter of combustion are therefore purely relative.* This may be proved by the following experiment:—

Let us hold a jar of hydrogen mouth downwards, and set fire to the hydrogen; it will burn at the mouth of the jar. Let us now quickly thrust a jet of oxygen into the jar: the oxygen will catch fire while passing the burning hydrogen, and will continue to burn within the jar.

Here we have a case of ordinary combustion at the mouth of the jar—the hydrogen being the combustible body and the air (*i.e.*, oxygen) being the supporter of combustion. But within the jar we witness a case of *reversed* or *inverted combustion*—the oxygen being the combustible, and the surrounding hydrogen being the supporter of combustion.

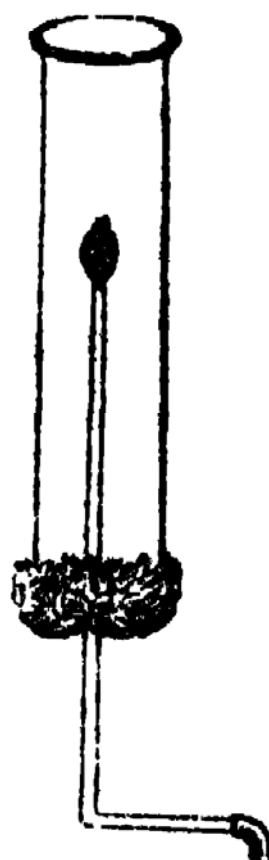


Fig. 18.

Similar experiments may be performed with other substances ordinarily called combustibles (*e.g.*, coalgas, alcohol, sulphur) and supporters of combustion (*e.g.*, chlorine, nitrous oxide).

Oxyhydrogen Blowpipe; Limelight.—The oxyhydrogen blowpipe is an apparatus in which hydrogen (or coalgas) is burnt in a stream of oxygen. The resulting flame gives very little light, but is intensely hot. It is used whenever a very high temperature is required, as in melting the metal platinum.

When an oxyhydrogen or oxy-coalgas flame is made to impinge on a cylinder of quick-lime, the substance becomes incandescent and emits a dazzling white light. This is known as *lime-light* or *Drummond light*, and is used in magic-lanterns and for other illuminating purposes.

Heat of Combustion.—When anything burns, a certain temperature is reached and a certain amount of heat is given out. If the combustion is rapid the temperature is high, and if the combustion is slow (as in the case of rusting of iron) there is no appreciable rise of temperature. But in both cases the amount of heat evolved is the same, when the same product is obtained by the combustion of a given quantity of any substance.

Kindling Temperature.—For every combustible substance there is a certain temperature which must be attained before it burns: this temperature is called the *kindling temperature* or *ignition point* of the substance. A substance does not burn when it is cooled down below its kindling temperature. The ignition point of some substances (e.g., liquid phosphoretted hydrogen) is below the ordinary temperature of the air: such substances are called *spontaneously inflammable*.

The Wire Gauze, and its use.—The fact that different bodies have different kindling temperatures is illustrated every day in our laboratory. When a piece of wire gauze is brought upon the flame of a bunsen burner, the flame spreads beneath the gauze and not above it. Again, when a piece of wire gauze is held a little over the top of the burner, and a lighted match is applied to the issuing gas above the gauze, the gas burns above and not below the gauze. In both these

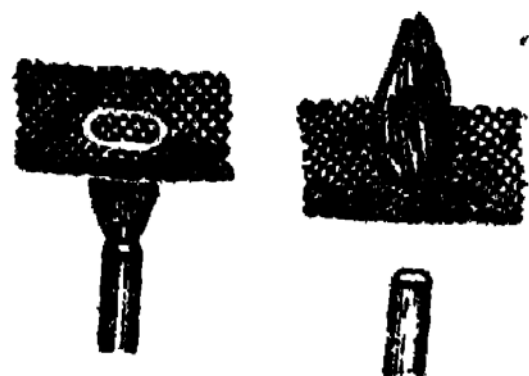


Fig. 19.

cases, *the flame does not pass on the other side of the gauze*: because, the heat of the burning gas is so rapidly dispersed away by the wire gauze that the gas on the other side of it does not attain its ignition point. If however, in the above cases, hydrogen were used instead of coalgas, the flame would have spread both above and below the gauze—the ignition point of hydrogen being lower than that of coalgas.

✓ **Davy's Safety-lamp.**—The safety-lamp, used by miners to avoid explosions of marsh-gas occurring in coal-pits, illus-

trates the principle of kindling temperature of gases. It is an ordinary oil-lamp, with its flame surrounded by wire gauze. When the lamp burns, the heat is so quickly conducted away by the wire gauze that the inflammable mixture of marsh gas and air outside the gauze cannot reach its kindling temperature; so that no serious explosion takes place.

✓ **The Flame, and its structure.**—A *flame* is a visible mass of intensely ignited gas or vapour. It marks the region where two gaseous bodies meet and combine with emission of heat and light. Solids and liquids do not burn with a flame until they are changed into vapour: for instance, in the case of candle-flame, the materials of the candle are first melted and then drawn up the wick and vaporized. Different substances have different kinds of flames. Thus, the flames of inflammable hydrocarbons are more or less luminous, whilst the flame of hydrogen emits intense heat but very little light.

The flame of a candle or coal-gas consists of four parts:—



(1) The dark central zone (A)—consisting of unburnt gases. This portion is hollow, *i.e.*, no combustion goes on here;* hence it is not properly a part of the flame.

(2) The luminous middle zone (B) of incomplete combustion—consisting of partially burnt gases and particles of carbon.† This is the region of light of the flame. This portion gets an insufficient supply of oxygen, and so exerts reducing action.

Fig. 20.

* 1. Insert one end of a narrow glass tube into the central zone; some of the unburnt gases will be drawn off at the other end of the tube, where they may be burnt.

2. Quickly thrust a lucifer-match into the central zone: the wood will be charred, but the match will not catch fire unless it touches the edges of the flame.

† Quickly depress a sheet of white paper horizontally into the flame, and remove it after a few seconds. Observe that a ring of soot (carbon) has been deposited on the paper, its centre remaining white.

(3) A small blue zone at the base of the flame, shading off into the mantle.

(4) The mantle or non-luminous outer zone (C) of complete combustion—consisting mainly of water-vapour and carbon dioxide. This is the region of heat of the flame. This portion has a full supply of oxygen, and exerts oxidizing action.*

✓ **Luminosity of Flames.**—The luminosity of a flame depends chiefly on the density of the burning gas and the presence of solid particles in it. Thus in ordinary oil-lamps the denser is the vapour produced and the richer is it with carbon, the greater is the light of the flame. The brilliancy of lime-light is due to the presence of the solid lime in the hot non-luminous oxyhydrogen flame.

✓ **The Bunsen Burner: Its parts.**—In this lamp, devised by Bunsen, coal-gas is suitably mixed with air before it is burned. The instrument consists of the following parts :

- (1) the side-tube (*s*) at the foot of the lamp, through which coal-gas is supplied ;
- (2) the jet or burner (*b*), from which the gas issues ;
- (3) the burner-tube (*t*), to the top of which the gas passes up mixed with air ;
- (4) the air-holes (*h*) at the base, through which air enters, but which may be



Fig. 21.

- partly or wholly closed by turning a ring surrounding them.

Its flame.—In the Bunsen burner, a complete combustion of the gas takes place owing to its being mixed up with air ; and so the flame is smokeless and non-luminous. The flame is blue and has high temperature ; it has no luminous middle zone. If, however, the air-holes are closed, the flame is smoky and luminous like an ordinary gas or candle flame.

* For the reducing and oxidizing powers of a flame see below.

Oxidation and Reduction.—When we strongly heat copper turnings in a current of air or oxygen, the metal is converted into cupric oxide. Here the metal combines with oxygen and is said to be *oxidised* or to undergo *oxidation*. The changes that take place when some other metals are heated in air (See pp. 7, 8) or anything is burnt in air or oxygen, as well as when iron rusts or vegetable and animal bodies decay slowly in air, are all examples of oxidation.

To study the opposite process, we put some cupric oxide in a bulb-tube (or in a porcelain boat placed within a hard glass tube), and pass dry hydrogen or carbon monoxide or coal-gas through the tube. When the gas has swept all the air out of the apparatus we light it at the jet of a connected



Fig. 22.

tube, and thus admitting a regular stream of the gas we heat the cupric oxide to redness: the black copper oxide is soon changed into red metallic copper. Ferric oxide and lead oxide, when similarly heated in a current of hydrogen, are changed into the metallic state. In these cases the oxides of the metals lose oxygen and are said to be *reduced* or to undergo *reduction*.

Properly speaking, *oxidation* means addition of oxygen to a substance, and *reduction* means withdrawal of oxygen from compounds containing it. The two terms are opposed but related: the oxidation of one substance often implies the reduction of another, as when carbon monoxide reduces cupric oxide and itself becomes carbon dioxide.

Substances which readily part with oxygen are called *Oxidising agents* or *Oxidisers*: such are oxygen, ozone, hydrogen peroxide, nitric acid, potassium chlorate, &c. On the other hand, substances which readily abstract oxygen are called *Reducing agents* or *Reducers*: such are hydrogen, carbon, carbon monoxide, coal-gas, sulphurous acid, &c.

NOTE.—Formerly, oxidation was used almost in the same sense as combustion. But now the words oxidation and reduction

are used in extended senses to include also changes in which elements similar to oxygen are added to or removed from substances. Thus, ores of metals are said to be 'reduced' when oxygen, sulphur, &c. are removed from the ores. So, chlorine is said to 'oxidize' sulphuretted hydrogen when they interact to form hydrogen chloride and sulphur.

Oxidizing and Reducing Blowpipe Flames.—The heating power of a flame is increased by blowing into it a current of air by means of a mouth blowpipe. To use the blowpipe with a Bunsen flame we close the holes of the burner and blow into the flame by means of the blowpipe, holding its nozzle or jet just at the edge of the flame. The flame is thus diverted and has (like the candle flame) two characteristic parts: (i) the inner part, which contains unburnt carbon and is yellow and luminous; (ii) the outer part, which has a free supply of air and is blue and non-luminous.

(1) When we direct a blowpipe flame over a metallic oxide so as to completely cover the oxide with the inner flame, the oxide is *heated in presence of carbon without access of air*: the oxide is thus *reduced* to the metallic state. The inner part of a blowpipe flame is accordingly called the reducing flame.

(2) On the other hand, when a suitable metal (*e. g.* lead or antimony) is held in the outer flame, the metal is *heated in an excess of air*: the metal is thus *oxidized*. The outer part of the blowpipe flame is therefore called the oxidizing flame.

NOTE.—The reducing flame is more prominent when we hold the nozzle of the blowpipe just outside the flame and blow gently; and the oxidizing flame is better produced when we blow harder by placing the nozzle of the blowpipe inside the flame.

University Examination Questions.

1. What is Combustion? [C. 97; A. 03]. Define the terms *burning* and *combustion* [C. 01].
2. Describe any experiment in which oxygen burns and hydrogen is a supporter of combustion [A. 03].
3. Describe the Davy Lamp. Is it always a safety lamp? Give reasons for your answer [A. 07]. Explain why the miner's

safety lamp can be carried safely in an explosive mixture of fire-damp and air [C. 07].

4. Explain the nature and composition of a flame. Discuss carefully upon what the luminosity of a flame depends [A. 04, 16]. What is a flame? Explain fully the structure of a candle flame, describing simple experiments in support of your explanation. Is there any difference between a candle flame and that of a Bunsen burner? If so, explain the nature and cause of the difference [C. 1912, 1916].

Give a full description (with diagrams) of a Bunsen burner, and explain how its mechanism influences the structure of the flame produced [C. 1910].

5. Explain the terms *oxidation* and *reduction* [C. 96, 1913; A. 96]. Describe experiments which you have done, illustrating oxidation and reduction [C. 09, 1913].

What is meant by the terms 'combustion' and 'oxidation'? Describe experiments to show the difference between the above two phenomena. [C. 1915].

Define the terms oxidizing agent and reducing agent. Classify the following substances as oxidizing or reducing agents, giving reasons in each case: (a) Hydrogen peroxide, (b) Nitric acid, (c) Sulphur dioxide, (d) Ferrous sulphate, and (e) Chlorine [A. 1910].

What is a *reducing agent*? Describe an experiment to illustrate its action [A. 98]. Mention various reducing agents [C. 96].

CHAPTER VII.

CHEMICAL EQUIVALENTS.

Equivalent or Combining Weight.—When we study the composition of different compounds we notice that chemical action takes place between elements in fixed proportions of their weights. For example, it is found by repeated experiments that 1 part of hydrogen combines with 8 parts of oxygen (to produce water), and with 35.5 parts of chlorine (to form hydrochloric acid); 8 parts of oxygen unite with 31.8 parts of copper (to form cupric oxide), and 35.5 parts of chlorine unite

with 23 parts of sodium (to form sodium chloride). Again 12 parts of magnesium displace 1 part of hydrogen (from hydrochloric acid), and 32.5 parts of zinc displace 31.8 parts of copper (from copper sulphate). These proportions of different elements, uniting with or displacing a constant amount of a third element (viz., 1 part of hydrogen, or 8 parts of oxygen, or 35.5 parts of chlorine), are said to be *equivalent* to one another.

It is found that hydrogen combines in smaller proportions by weight than any other element, *i.e.* hydrogen has the smallest equivalent weight. So, for the sake of convenience, we take a unit mass of hydrogen as the standard for fixing the equivalents of other elements. The Equivalent or Combining Weight of an element is therefore defined as *the smallest weight of the element which combines with or displaces unit quantity of hydrogen.*

Determination of Equivalents.—The methods of determining equivalents vary according to the nature of the element. Generally, we may either analyse or synthetically produce a compound of the element with hydrogen, and thus ascertain what amount of the element combines with one part of hydrogen. But there are many elements which neither combine with hydrogen nor displace it from an acid; so their equivalents are found by ascertaining the quantities which combine with or displace the known equivalent of some other element, as oxygen or chlorine. Some typical examples are given below.

Equivalent of Oxygen.—By carefully studying the composition of water it has been found that 100 parts of water contain nearly 88.9 parts of oxygen and 11.1 parts of hydrogen.

11.1 parts of hydrogen combine with 88.9 parts of oxygen.

∴ 1 part „ „ combines „ $\frac{88.9}{11.1}$ „ „ „

Hence, the equivalent of oxygen is $\frac{88.9}{11.1} = 8$ nearly.

Equivalent of Chlorine.—It has been determined from the composition of hydrochloric acid gas that it contains

Equivalent of Copper.—This may be determined by reducing cupric oxide by means of hydrogen or coal-gas :

Weigh a small porcelain boat ; put in it a gram of black copper oxide, and weigh again. Place the boat with the oxide in a hard glass tube, and pass hydrogen or coal-gas through the tube (Fig. 22). When all the air in the apparatus has been driven out, heat the oxide to redness, whilst still passing the gas. The gas will reduce the oxide to metallic copper. When the boat has cooled, take it out and weigh again.

Calculate the results as follows—

Second weighing.....16 gr.=weight of boat+cupric oxide

First " 15 " = weight of boat

Difference ... 1 gr. = weight of cupric oxide.

Third weighing ... 15·8 gr.=weight of boat+copper

First " ... 15·0 " = weight of boat

Difference ... 0·8 gr. = weight of copper.

Hence, in 1 gr. of cupric oxide there is ·8 gr. of copper.

That is, $(1 - \cdot 8) = \cdot 2$ gr. of oxygen combines with ·8 gr. of copper.

\therefore 8 gr. of oxygen combine with $\frac{8 \times \cdot 8}{2} = 32$ gr. of copper.

That is, the equivalent of copper is 32.

More exact determinations give us the value 31·8.

Equivalent of Zinc.—This may be determined by converting zinc into its oxide by means of nitric acid :

Weigh a porcelain crucible with its lid. Put in it about a gram of clean pieces of zinc foil, and weigh again. Add to it strong nitric acid drop by drop, till all the zinc is dissolved. Carefully evaporate the residue (zinc nitrate and water) to dryness, and then heat it strongly (so as to convert the nitrate into zinc oxide). When the crucible has cooled, weigh it with its contents,

Calculate the results as follows—

Second weighing ...26·27 grams=weight of crucible+zinc

First " ...25·46 " = " " crucible

Difference... 0·81 gram = " " zinc

Third weighing ...26·47 grams=weight of crucible+zinc oxide

Second " ...26·27 " " " crucible+zinc

Difference... 0.20 gram = ,, ,, oxygen that combines with
0.81 gram of zinc.

Hence, the weight of zinc uniting with 8 grams of oxygen is
 $\frac{0.81 \times 8}{2} = 32.4$ grams.

That is, the equivalent of zinc is 32.4 nearly.

The equivalents of copper, tin, lead, etc. may be found by this method.

Equivalent of Sodium.—This may be found by ascertaining what weight of sodium combines with the equivalent weight of chlorine :

Weigh a porcelain dish. Put in it a little quantity of clean sodium cut up into small pieces, and *quickly* weigh again. Remove the sodium, pour some water in the dish, and gradually add the pieces of sodium. When all the sodium has dissolved, add enough hydrochloric acid. Evaporate the resulting product (sodium chloride and water) to dryness, and reweigh the dish with its contents (sodium chloride).

The results may be thus calculated—

Second weighing... 20.58 grams = weight of dish + sodium

First ,, ... 20.37 ,, = ,, ,, dish

Difference... 0.21 gram = ,, ,, sodium

3rd weighing... 20.904 grams = weight of dish + sodium chloride

2nd ,, ... 20.580 ,, = weight of dish + sodium

Difference... 0.324 gram = ,, ,, chlorine which unites with
0.21 gram of sodium.

Hence, the weight of sodium combining with 35.5 grams of chlorine
is $\frac{35.5 \times 0.21}{0.324} = 23$ grams nearly.

That is, the equivalent of sodium is 23 nearly.

University Examination Questions.

1. Explain what you understand by the *combining weight* of an element. Illustrate by examples. [C. 95, 99]. Explain what is meant by equivalent weight [C. 04 ; A. 03, 09, 1910].

2. How should you determine any equivalent weight ? [A. 06]. Give details of any experiment you have made or seen for the approximate determination of the equivalent of an element [A. 1910].

3. How may the equivalent weights of such substances as (1) oxygen and (2) copper be determined? [A. 09].

Find the equivalent weights of oxygen and copper from the data given below:—Dry hydrogen is passed over 1.58 grams of heated copper oxide, the water formed weighs 0.36 grm., the weight of copper left after the experiment is 1.26 grms. [A. 02].

4. If 465 ccs. of hydrogen at NTP are obtained by the action of .5 grams of magnesium on excess of hydrochloric acid, what is the equivalent of magnesium? [A. 03].

164 milligrams of a metal dissolved in hydrochloric acid evolve 31 c.c. of hydrogen at N. T. P. ; calculate the equivalent weight of the metal [C. 05].

0.1 gram, of a metal gave on treatment with a dilute mineral acid 34.2 c.c. of Hydrogen measured at N.T.P. Calculate the equivalent weight of the metal. [C. 1915].

5. Describe how you would proceed to determine the equivalent of zinc. [C. 09].

6. Describe an experiment to determine the equivalent of tin by its conversion into oxide by means of nitric acid [C. 04].

CHAPTER VIII.

LAWS OF COMBINATION: ATOMIC THEORY AND AVOGADRO'S HYPOTHESIS.

Laws of Chemical Combination.—The Laws of Combination are generalized statements of the invariable relations between the proportions in which elements are observed to participate in chemical changes. The following are the four laws, of which the first three refer to the *weights* of substances, while the fourth relates to the *volumes of gases* only:

1. **Law of Definite or Constant Proportions.**—*The same compound is always composed of the same elements united together in the same proportion.* In other words, “chemical combination always takes place between definite masses of substances.” For example, water is a compound of the ele-

ments hydrogen and oxygen : from whatever source we may obtain it whether as rain, or from river or spring and by whatever method we may prepare it artificially, water will always be found to consist of 1 part by weight of hydrogen and 8 parts by weight of oxygen. If we try to combine, say 4 parts of hydrogen with 8 parts of oxygen, combination will take place between the elements in the required proportion, and 3 parts by weight of hydrogen will be left unaltered.

II. Law of Multiple Proportions.—*When the same two elements form more than one compound, the different quantities of one element which combine with a fixed quantity of the other, bear a simple multiple relation.* Thus hydrogen and oxygen combine in two different proportions giving rise to the two compounds Water and Hydrogen peroxide : in water there are nearly 1 part of hydrogen and 8 parts of oxygen ; while the latter contains 1 part of hydrogen and 16 parts of oxygen. The quantities of oxygen which unite in these cases with the same weight of hydrogen, bear to each other the ratio of 8 : 16, that is 1 : 2.

The two elements oxygen and nitrogen combine in five different proportions forming as many different compounds, the names and approximate compositions of which are these :

- | | |
|-------------------------|---|
| (1) Nitrogen monoxide— | 28 parts of nitrogen and 16 parts of oxygen |
| (2) Nitrogen dioxide— | „ „ „ „ „ 32 „ „ „ |
| (3) Nitrogen trioxide— | „ „ „ „ „ 48 „ „ „ |
| (4) Nitrogen peroxide— | „ „ „ „ „ 64 „ „ „ |
| (5) Nitrogen pentoxide— | „ „ „ „ „ 80 „ „ „ |

Here the weights of oxygen combining with the same weight of nitrogen are in simple multiple ratios, *viz.*, 16 : 32 : 48 : 64 : 80, *i. e.*, 1 : 2 : 3 : 4 : 5.

III. Law of Reciprocal or Equivalent Proportions.—*The quantities of different elements which separately combine with a constant quantity of a third element, are either the same as or are simple multiples of the quantities of these different elements when they combine amongst themselves.* For example nearly 35.5 parts of chlorine and 127 parts of iodine separately combine with 1 part of hydrogen (forming respectively

hydrochloric acid and hydriodic acid): 35.5 parts of chlorine and 127 parts of iodine also unite with each other (forming iodine monochloride).

Again, both carbon and sulphur combine with oxygen, forming compounds of the following compositions—

Carbon dioxide—nearly 32 parts of oxygen and 12 parts of carbon

Sulphur dioxide— „ „ „ „ „ „ 32 „ „ „

But carbon and sulphur combine with each other (forming carbon disulphide) in the proportion of 12 parts carbon to 64 parts sulphur. Hence, the proportion by weight (12 : 32) in which carbon and sulphur separately combine with the same weight of oxygen, is a simple multiple (*i.e.*, double) of the proportion (12 : 64) in which they combine with each other.

IV. Gay-Lussac's Law of Gaseous Volumes.—The volumes in which gases combine bear a simple relation to one another, and to the volume of the gas produced. For example, 2 volumes of hydrogen combine with 1 volume of oxygen and form 2 volumes of steam. Similarly, 1 volume of hydrogen combining with 1 volume of chlorine produces 2 volumes of hydrochloric acid gas. Again, by decomposing 2 volumes of ammonia we get 1 volume of nitrogen and 3 volumes of hydrogen.

Dalton's Atomic Theory.—To explain the Laws of Chemical Combination, the great scientist Dalton made certain hypotheses or assumptions which are now embodied in what is called the Atomic Theory. The theory may be stated thus :—(1) *All things are made up of minute indivisible particles, called Atoms*; (2) *the atoms of the same element are all alike in weight and other properties, but differ from the atoms of every other element*; (3) *atoms of different elements attract one another, and chemical combination consists in the juxtaposition or union of the atoms.*

The Atomic Theory satisfactorily explains the Laws of Definite and Multiple Proportions on which however the theory was originally based. The Law of Equivalent Proportions follows from these two primary laws.

Explanation of the Law of Definite Proportions.—Let us consider the case of a compound of hydrogen and chlorine. According to the Atomic Theory, combination takes place between the atoms of these elements, and the weight of an atom of each element is fixed. Suppose, one atom of hydrogen combines with one atom of chlorine: then the resulting compound will contain equal numbers of hydrogen atoms and of chlorine atoms; and the ratio between the total weights of these atoms will be the same as the ratio between the weights of the single atoms. That is to say, the compound will always have a definite composition.

Explanation of the Law of Multiple Proportions.—Let us take the case of carbon and oxygen, which form two different compounds. Suppose, the first compound contains the elements in the proportion of 1 atom of carbon to 1 atom of oxygen. Now, if the second compound contains more of oxygen, there must be *at least* 1 atom more of it (because, according to the Atomic Theory, there cannot be a fraction of an atom) combined with every 1 atom of carbon. That is to say, every particle of this compound will contain 1 carbon atom and 2 oxygen atoms. Hence, in the second compound the amount of oxygen will be double of that contained in the first.

Atoms and Molecules.—Chemists suppose, following Dalton, that every *element* consists of extremely small *indivisible* particles which they call *Atoms*. The atoms of the same element are exactly alike in their properties, but atoms of different elements have different properties. Atoms seldom exist singly, but two or more of them form a small cluster called a *Molecule* (=a small mass). A molecule of an element consists of similar atoms, while a molecule of a compound is composed of different kinds of atoms. It follows therefore that *the weight of a molecule is the sum-total of the weights of the constituent atoms*.

The difference between an atom and a molecule will be clear from an illustration. Suppose we go on dividing and sub-

dividing a drop of water (which, we know, is made up of oxygen and hydrogen). We may carry on the process of division to the utmost limit, until we have a particle of water so small that on further division it ceases to be water and breaks up into two atoms of hydrogen and one atom of oxygen. This smallest particle which can exist as water is its molecule.

An Atom is defined as the smallest portion of an element that can take part in a chemical change, i.e., in the formation of a chemical compound. A Molecule is the smallest portion of an element or of a compound that can be supposed to have separate existence.

Avogadro's Law.—To account for Gay-Lussac's Law of combination of gases by volume, Avogadro suggested that *at the same temperature and pressure, equal volumes of all gases contain equal number of molecules.* The hypothesis means that when at some fixed temperature and pressure the same vessel is successively filled with different gases (whether elementary or compound or mixtures like air), the vessel will contain an equal number of molecules in all cases. In other words, the molecules of all gases have equal volumes or occupy the same space.

Conclusions from Avogadro's Law.—Avogadro's Law explains how different gases are equally affected in volume for alterations of pressure and temperature (Laws of Boyle and Charles). The hypothesis also leads to the following important conclusions :—

1. Of the Constitution of Hydrogen Molecule.—It is found by experiment that when 1 volume of hydrogen unites with 1 volume of chlorine, 2 volumes of hydrogen chloride are produced. Supposing there are m number of molecules in 1 volume of hydrogen, it follows from Avogadro's Law that there are $2m$ number of molecules in 2 volumes of hydrogen chloride. Now, as each molecule of hydrogen chloride must contain at least 1 atom of hydrogen, $2m$ molecules of hydrogen chloride will contain $2m$ atoms of hydrogen, and these were contained in m number of hydrogen molecules.

Therefore, *each molecule of hydrogen is made up of two atoms.* [It follows by the same reasoning that a molecule of chlorine contains two atoms]. Hence, if the weight of an atom of hydrogen is taken as 1, the weight of a molecule of it is 2.

2. Of the relative Weights of Gaseous Molecules.—As equal volumes of gases contain the same number of molecules, the weights of equal volumes of gases (and so their densities) must be proportional to the weights of their respective molecules. Now, as the density of a gas is referred to hydrogen as unit, we have the proportion—

$$\begin{aligned} &\text{Density of any gas : molecular weight of the gas} \\ &= \text{Density of hydrogen : molecular weight of hydrogen} = 1 : 2. \end{aligned}$$

Hence, *the molecular weight of a gas is double of its density.*

Knowing therefore the density of a gas (pp. 18, 19), we can find its molecular weight by doubling the number expressing the density. A knowledge of molecular weights thus arrived at from Avogadro's Law, is of great help to us in determining Atomic Weights. [See next chapter].

3. Of the Volumes of Gaseous Molecules.—We do not know what volume is occupied by an atom or a molecule. For the sake of convenience, chemists speak of an atom of hydrogen as occupying 1 volume; a molecule of hydrogen would thus occupy 2 volumes. But, according to Avogadro's Law, the molecular volume of hydrogen is the same as that of any other gas. Hence, *a molecule of any gas occupies 2 volumes.*

4. Of the Combination of Gases by Volume.—Avogadro's Law states that the molecule of all gases have equal volumes. It follows therefore that the volumes of gases taking part in (and resulting from) chemical changes, are proportional to the numbers of the respective molecules of the gases. This conclusion is important in two respects—

(a) It tells us the comparative volumes of the gases when the molecular equation is known. For example, if we know that 2 molecules of hydrogen unite with 1 molecule of oxygen to produce 2 molecules of steam, it becomes evident

that the respective volumes of the three gases are also in the same ratio. Gay-Lussac's Law is thus explained by Avogadro's hypothesis. [See Calculation of Volumes, Chap. XII].

(b) It enables us to fix the molecular formula of a gaseous compound when we know its volumetric composition and density. [See, under Composition of Ammonia, Oxides of Nitrogen and of Carbon, &c].

University Examination Questions.

1. State and explain with illustrations the laws of chemical combination [C. 94, 1911; A. 05].

2. Explain the laws of chemical combination in definite and multiple proportions. Give examples [C. 91, 09; A. 14]. Chemical combination always takes place between definite masses of matter. Explain what you understand by this statement and illustrate your reply by examples [C. 93]. State and explain the law of multiple proportions, and illustrate it by at least three examples [A. 07]

3. State any laws relating to the combination of gases by volume [A. 03].

Define the law of gaseous volumes, and illustrate it by experiments. What hypothesis was propounded to account for the facts underlying the law? [C. 1915].

Nitrogen, oxygen and chlorine all combine with hydrogen, but their proportions by volume in which they combine with that element are 3 : 1, 2 : 1 and 1 : 1. Explain the theory which this fact has given rise to [A. 02].

4. What is the Atomic Theory? State the consideration which led to its enunciation as an hypothesis [C. 96]. Give a short account of Dalton's Atomic Theory and state how it explains the two primary laws of chemical combination [C. 92]. What relation do the laws of chemical combination bear to the atomic theory? [C. 1911].

5. Define the terms atom and molecule [C. 01]. What is the difference between an atom and a molecule [A. 93].

6. What is Avogadro's Law? [C. 98, 02; A. 93, 08]. State Avogadro's Hypothesis, and show the important bearing that this hypothesis has upon the science of Chemistry [C. 1910; A. 04]. Explain Avogadro's Law, and indicate how it has helped in the development of the Atomic Theory [C. 1914].

What is the difference between a molecule and an atom of hydrogen [C. 98.] A molecule of hydrogen is said to consist of two atoms. Give reasons for the truth or otherwise of the statement [A. 02.]

State Avogadro's hypothesis, and prove with its aid that the molecules of hydrogen and oxygen must contain at least two atoms. [A. 1912].

Explain clearly how Avogadro's Law helps us to determine molecular weights [A. 08]. Explain the relationship between the molecular weight and the relative density of a gas [C. 01].

Enunciate Avogadro's Law, and explain its importance in determining the atomic weights of elements, illustrating your answer by examples [C. 1916].

CHAPTER IX.

ATOMIC AND MOLECULAR WEIGHTS.

Atomic Weight and Molecular Weight.—These words literally mean respectively the weight of an atom and of a molecule of any substance. But as no atom or molecule can be seen (even with the aid of the most powerful microscope) and weighed, we cannot determine the *absolute* weight of any single atom or molecule. We can only determine the *relative* weight, by ascertaining how many times an atom or a molecule of a substance is heavier than an atom of a standard substance. Hydrogen being the lightest substance the weight of an atom of it is represented as 1, and the weights of atoms and molecules of other substances are expressed in terms of this unit.

The Atomic Weight of an element is the number which expresses how many times is its smallest portion that can take part in a chemical change heavier than such smallest portion of hydrogen. The Molecular Weight of a substance is the weight of its smallest particle capable of separate existence, as compared with the weight of an atom of hydrogen (represented as unity).

For example, when we say that the atomic weight of oxygen is 16, we mean that the atom of oxygen is 16 times heavier than the hydrogen atom. Similarly, when we say the molecular weight of oxygen is 32, and of water 18, we mean that a molecule of oxygen is 32 times heavier than an atom of hydrogen, and that a molecule of water is 18 times as heavy as the hydrogen atom. It is clear that a compound has molecular weight only, while an element can have both atomic and molecular weights.

Determination of Atomic Weight.—There is no general rule for finding the atomic weight of an element. Chemists ascertain the approximate atomic weight of an element by one or more of various methods, the chief considerations being its chemical equivalent, vapour densities of its compounds, and its specific heat. [For another method, based on *isomorphism*, see p. 42].

1. **Purely Chemical Method.**—In this method the chemical equivalent of an element is chiefly taken into account. Suppose we are to find the atomic weight of oxygen. The proportion by weight in which oxygen unites with hydrogen to form water is 8 : 1. Now, it has been ascertained by careful experiments that when water is acted upon by sodium, all the oxygen contained in the water at once unites with sodium, while the hydrogen is evolved in equal quantities in two stages. It follows therefore that to *every* atom of oxygen there are *two* atoms of hydrogen; and as their relative proportions by weight are nearly 8 : 1, the atomic weight of oxygen is 16.

2. **Method based on Vapour Densities of Compounds.**—The atomic weight of an element is ascertained by studying the composition of its gaseous or volatile compounds with reference to their molecular weights (which we know by Avogadro's Law to be double of their vapour densities). The least quantity of the element present in a molecular amount of the various compounds, is the atomic weight of the element. For

example, the atomic weight of oxygen may be determined from experimental results tabulated thus—

Compound.	Molecular Weight.	Weights of Constituents in a molecular amount.					
		Hydrogen.	Nitrogen.	Carbon.	Sulphur.	Phosphorus.	Oxygen.
Water ...	18	2	16
Nitrous oxide ...	44	...	28	16
Carbon dioxide ...	44	12	32
Sulphur dioxide ...	64	32	...	32
Phosphoric anhydride	284	124	160

In these molecules of five compounds the weights of oxygen, as compared with the weight of 1 atom of hydrogen, are 16, 16, 32, 32, 160. The lowest number of the series by which all the numbers are exactly divisible is 16. Hence, the atomic weight of oxygen is 16.

NOTE.—The constitution of molecules of elements becomes evident on comparing the atomic with the molecular weights ; *e.g.*—

(a) The molecular weights of sodium, potassium, zinc, and mercury are *equal* to their atomic weights. The molecules of these elements consist of only 1 atom.

(b) The molecular weights of hydrogen, oxygen, nitrogen, sulphur, and the halogens are *double* of their atomic weights. Their molecules consist of 2 atoms.

(c) The molecular weight of phosphorus is *four times* its atomic weight. Its molecule consists of 4 atoms.

3. Method based on Specific Heats of Solids.—It is found that equal weights of different substances require different amounts of heat to be raised through the same range of temperature. This is expressed by saying that different substances have different *thermal capacities* or *specific heats*.

For example, the amount of heat required to raise a certain quantity of water from 0° to 100° is nearly 30 times as much as that required to heat the same quantity of mercury or platinum to the same extent. As water has the greatest thermal capacity, the amount of heat required to raise 1 gram of water from 0° to 1°C is taken as the standard for comparing the specific heats of other substances. The specific heat of a substance is therefore never greater than 1; and is defined as the ratio between the amount of heat required to raise a unit mass of the substance through 1° and that required to raise the same mass of water through 1° .

Dulong and Petit's Law.—From observations of the specific heats of different solids, Dulong and Petit discovered the law that the specific heats of solid elements are inversely proportional to their atomic weights. In other words, the capacities for heat of the atoms of elements in the solid state are equal. This law is found to be true in most cases: the product of the specific heat and the atomic weight of a solid element, is nearly equal to the constant number 6.4. Thus—

<i>Element.</i>	<i>Specific heat.</i>		<i>Atomic weight.</i>	
Zinc	.093	\times	65	$= 6.1$
Iron	.112	\times	56	$= 6.3$
Mercury	.032	\times	200	$= 6.4$
• Potassium	.166	\times	39	$= 6.5$
Sodium	.29	\times	23	$= 6.7$

Roughly speaking, specific heat \times atomic weight $= 6.4$. Hence Dulong and Petit's Law is applied with advantage in determining or verifying the atomic weights of elements. Suppose, the specific heat of a solid element as determined experimentally is S , its atomic weight is then approximately $\frac{6.4}{S}$.

Table of Atomic Weights.—The following is a list of

the more important and common elements (with their symbols) arranged in order of their approximate atomic weights :—

Elements.	Symbols.	Atomic Weights.	Elements.	Symbols.	Atomic Weights.
Hydrogen ...	H	1	Iron ...	Fe	56
Lithium ...	Li	7	Nickel ...	Ni	58·6
Boron ...	B	11	Copper ...	Cu	63·6
Carbon ...	C	12	Zinc ...	Zn	65·3
Nitrogen ...	N	14	Arsenic ...	As	75
Oxygen ...	O	16	Bromine ...	Br	80
Fluorine ...	F	19	Strontium ...	Sr	87·6
Sodium ...	Na	23	Silver ...	Ag	108
Magnesium ...	Mg	24·2	Tin ...	Sn	119
Aluminium ...	Al	27	Antimony ...	Sb	120
Silicon ...	Si	28·3	Iodine ...	I	127
Phosphorus ...	P	31	Barium ...	Ba	137·4
Sulphur ...	S	32	Platinum ...	Pt	195
Chlorine ...	Cl	35·5	Gold ...	Au	197
Potassium ...	K	39	Mercury ...	Hg	200
Calcium ...	Ca	40	Lead ...	Pb	207
Manganese ...	Mn	55	Bismuth ...	Bi	208

University Examination Questions.

1. Define the terms atomic weight and molecular weight [C. 01 ; A. 10]. What is the difference between the atomic weight and the molecular weight of an element ? [A. 93].
2. Mention and explain *shortly* any two of the methods that may be employed to find out Atomic Weights [A. 08].
3. How would you determine the relative weights of a molecule of hydrogen, and one of chlorine, pointing out clearly all the steps in the process ? Also mention what assumptions are made. [A. 94].
4. State the relative weights of the molecules of oxygen, phosphorus, hydrogen, and ammonia [C. 02].
5. What connection exists between the specific heats of elements in the solid state and their atomic weights ? [A. 05, 10, 12].
6. Give a very brief outline of any method for the determination of the atomic weight of an element. A metallic oxide was found to contain 47·06 per cent. of oxygen. What is the exact atomic weight of the metal and what is the formula of the oxide ? The specific heat of the metal = 0·225, and the atomic weight of oxygen = 16. [A. 1914].

CHAPTER X.

SYMBOLS AND FORMULÆ.

Symbols.—A symbol is an abbreviation for the full name of an element, and represents one atom of the element. Thus, H means an atom of Hydrogen, S stands for an atom of Sulphur. Generally the symbol of an element is the initial letter of its English or Latin name. But when the names of two or more elements begin with the same letter, the symbol of a particular element is composed of the initial letter and another prominent letter; thus, B being the symbol of boron, Ba is the symbol of barium, Bi of bismuth, Br of bromine, and so on.

As the molecule of an element generally consists of a number of atoms, it is expressed by placing the particular numeral after the symbol of the atom. Thus, H_2 means a molecule of hydrogen consisting of two atoms, P_4 denotes a molecule of phosphorus composed of four atoms, and so forth. The molecule of an element thus expressed symbolically is often called the *Formula* of the element.

Formulae.—A formula is the symbolic representation of a molecule of a compound substance. It is constructed by grouping together the symbols of the constituent elements, the proportions of the elements being expressed by attaching numerals to the symbols. Thus the formula of a molecule of water (which consists of two atoms of hydrogen and one atom of oxygen) is H_2O . Similarly, $NaCl$ is the formula of common salt (consisting of one atom of sodium and one atom of chlorine); sulphuric acid is composed of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen, and is therefore expressed by the formula H_2SO_4 . In order to express two or more molecules of a substance we place numerals before the formula; as, $2H_2O$, $3H_2O$, &c.

A formula thus expresses the exact composition of a substance. It shows us (1) *qualitatively*, what elements unite to

form a particular compound, and (2) *quantitatively*, how many atoms of each of the elements are present in every molecule of the compound.

Percentage Composition.—By this is meant the number of parts (or proportions by weight) of each of the elements present in 100 parts of a compound. The percentage composition of a compound is ascertained by analysing it.

Determination of Formulae from Percentage Composition.—Knowing the percentage composition of a compound we can ascertain its formula. The rule is this :—*Divide the percentage of each element by its atomic weight and then divide these quotients by the lowest of them.* By so doing we ascertain the proportionate number of atoms of each element present in the compound, and thus obtain its *simplest* or *empirical formula*. Hence we can deduce the *molecular formula* when the density of the compound is known.

EXAMPLE 1. *To find the formula of a substance which is found on analysis to contain the following :—*

Sodium	27.38
Hydrogen	1.19
Carbon	14.29
Oxygen	57.14
<hr/>			
Total			100

Dividing the percentage of each element by its atomic weight we get

$$\text{Sodium (Na)} \quad \dots \quad \frac{27.38}{23} = 1.19$$

$$\text{Hydrogen (H)} \quad \dots \quad \frac{1.19}{1} = 1.19$$

$$\text{Carbon (C)} \quad \dots \quad \frac{14.29}{12} = 1.19$$

$$\text{Oxygen (O)} \quad \dots \quad \frac{57.14}{16} = 3.57$$

Dividing these numbers by the lowest, we get the ratio between the number of the atoms as follows—

$$\frac{1.19}{1.19} = 1 = \text{Na} ; \quad \frac{1.19}{1.19} = 1 = \text{H} ; \quad \frac{1.19}{1.19} = 1 = \text{C} ; \quad \frac{3.57}{1.19} = 3 = \text{O}_3.$$

Hence the simplest formula of the compound is NaHCO_3 .

EXAMPLE 2. *To find the formula of a substance having the following composition :—Fe = 20.15%, S = 11.51%, O = 23.02% and H_2O = 45.31%.*

Dividing the percentages of the three elements by their atomic weights, and that of water by its molecular weight, we get

$$\frac{20.15}{56} = .36 \text{ of Fe} ; \quad \frac{11.51}{32} = .36 \text{ of S} ; \quad \frac{23.02}{16} = 1.44 \text{ of O} ;$$

$$\text{and } \frac{45.31}{2 \times 1 + 16} = 2.52 \text{ of } \text{H}_2\text{O}.$$

Dividing these numbers by the lowest we get—

$$\frac{.36}{.36} = 1 = \text{Fe} ; \quad \frac{.36}{.36} = 1 = \text{S} ; \quad \frac{1.44}{.36} = 4 = \text{O}_4 ; \quad \frac{2.52}{.36} = 7 = 7\text{H}_2\text{O}.$$

Hence the formula is $\text{FeSO}_4, 7\text{H}_2\text{O}$.

EXAMPLE 3. *To find the formula of a compound whose vapour density is 30, and which consists of carbon 40 per cent., hydrogen 6.6 per cent., and oxygen 53.4 per cent.*

Dividing the numbers by the respective atomic weights, we get $\frac{40}{12} = 3.3$ of carbon, $\frac{6.6}{1} = 6.6$ of hydrogen, $\frac{53.4}{16} = 3.3$ of oxygen.

Reducing these numbers to the simplest ratio, we have

$$\frac{3.3}{3.3} = 1 = \text{C}, \quad \frac{6.6}{3.3} = 2 = \text{H}_2, \quad \frac{3.3}{3.3} = 1 = \text{O}.$$

Hence, the simplest formula is CH_2O .

Now, the vapour density of the substance being 30, its molecular weight must be $30 \times 2 = 60$. If, however, its molecular formula were CH_2O , its molecular weight would have been $12 + (1 \times 2) + 16 = 30$. Hence, in order that its molecular weight be 60, its molecular or true formula must be double of its simplest formula, i. e., $\text{C}_2\text{H}_4\text{O}_2$.

Determination of Percentage Composition from Formula.—It is very easy to calculate the percentage composition of a compound when its formula is known. Let us find out, for example, the percentage composition of sulphuric acid (H_2SO_4).

We are first to find out its molecular weight (which is equal to the sum of the weights of the constituent atoms)—

$$\begin{array}{rcl} \text{H}_2 & = 1 \times 2 & = 2 \\ \text{S} & & = 32 \\ \text{O}_4 & = 16 \times 4 & = 64 \\ \hline & & 98 \end{array}$$

Hence, we find that 98 parts (grams, ounces, or pounds) of H_2SO_4 contain 2 parts of hydrogen, 32 parts of sulphur, and 64 parts of oxygen. From these we are to calculate what parts of these elements are contained in 100 parts of H_2SO_4 —

$$98 : 100 :: 2 : x; \text{ or } x = \frac{100 \times 2}{98} = 2.04 \text{ of H}$$

$$98 : 100 :: 32 : y; \text{ or } y = \frac{100 \times 32}{98} = 32.65 \text{ of S}$$

$$98 : 100 :: 64 : z; \text{ or } z = \frac{100 \times 64}{98} = 65.31 \text{ of O}$$

Total 100 parts of H_2SO_4

University Examination Questions.

1. A substance has the following percentage composition; what is its formula?—Oxygen, 38.1; Hydrogen, 0.8; Phosphorus, 24.6; Sodium, 36.5. [A. 01, 08].

2. The percentage composition of a chemical compound is :—O=58.52, H=2.48, S=39. Find out its formula [C. 08].

3. Calculate the empirical formulæ of the substances that have the following percentage composition :—

(a) Carbon=69.76, Hydrogen=11.62, and Oxygen=18.61.

(b) Magnesium=21.62, Phosphorus=27.93, and Oxygen=50.45. [A. 08].

A substance contains—Carbon 32, Hydrogen 4, Oxygen 64. Find its simplest formula. [A. 1911].

CHAPTER XI.

VALENCY OR ATOMICITY.

Quantivalence or Valency.—Elements differ in their power of combining with one another; and chemists measure the combining power of an element in terms of the number of atoms of hydrogen with which an atom of the element can combine. Thus, 1 atom of chlorine combines with 1 atom of hydrogen (as in HCl), 1 atom of oxygen holds in combination 2 atoms of hydrogen (as in H_2O), 1 atom of nitrogen unites with 3 atoms of hydrogen (as in NH_3), and so on. The combining capacity of chlorine is then 1, that of oxygen 2, and that of nitrogen 3. This combining power of an element is called its *atom-fixing power* or *atomicity*, *quantivalence* or *valency*.

When an element does not combine with hydrogen, its combining capacity is measured with reference to chlorine (or some other monovalent element) with which it enters into combination. The valency of an element, then, means its combining value, as measured by the maximum number of atoms of hydrogen (or some other monad) with which one atom of the element can combine.

Classification of Elements according to Valency.—Elements are divided, according to their valency, into six classes. Some unite with hydrogen (or chlorine) atom for atom, and are called *monovalent* or *monad* elements. An element, one atom of which unites with two atoms of hydrogen (or chlorine), is called *divalent* or *dyad*. Similarly, there are *trivalent* or *triad*, *tetravalent* or *tetrad*, *pentavalent* or *pentad*

and *hexavalent* or *hexad* elements. The common elements are classified in the following table :—

Monovalents or Monads.	Divalents or Dyads.	Trivalents or Triads.	Tetravalents or Tetrads.	Pentavalents or Pentads.	Hexavalents or Hexads.
Hydrogen	Oxygen	Boron	Carbon	Nitrogen	Sulphur
Fluorine	Calcium	Aluminium	Silicon	Phosphorus	Manganese
Chlorine	Strontium	Iron	Platinum	Arsenic	
Bromine	Barium	Gold	Tin		
Iodine	Magnesium	Bismuth			
Potassium	Zinc				
Sodium	Mercury				
Silver	Copper				
	Lead				

It is evident that 1 atom of a tetrad is equal in combining value to 2 atoms of a dyad, as in carbon dioxide (CO_2); 1 atom of a hexad unites with 3 atoms of a dyad, as in sulphur trioxide (SO_3). Similarly, 2 atoms of a triad are equal to and unite with 3 atoms of a dyad, as in boron trioxide (B_2O_3); and 2 atoms of a pentad are equal to 5 atoms of a dyad, as we have in phosphorus pentoxide (P_2O_5).

Relation of Equivalent, Atomic Weight, and Valency.—Remembering what we mean by the equivalent weight and atomic weight of an element, we find that—

The atomic weight of a monad = its equivalent weight

“ “ “ “ dyad = $2 \times$ “ “ “

“ “ “ “ triad = $3 \times$ “ “ “

Hence, generally, Atomic Weight = Valency \times Equivalent

or, Equivalent = $\frac{\text{Atomic Weight}}{\text{Valency}}$

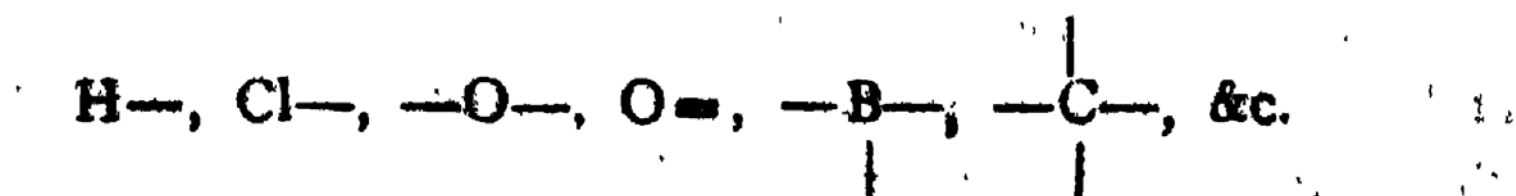
Variation of Valency.—In some cases the valency of an element varies. For example, nitrogen acts both as a triad (as in NH_3) and as a pentad (as in NH_4Cl); sulphur is divalent (as in SH_2), tetravalent (as in SO_2), and hexavalent (as in SO_3); carbon is both divalent (as in CO) and tetravalent

(as in CO_2). In such cases of variation, the valency of an element is generally represented by the highest number of monovalent atoms with which an atom of the element can combine; thus nitrogen is regarded as a pentad, carbon as a tetrad, and so on.

In most cases, the active valency of an element whose valency varies is found to increase or diminish by 2. Elements (*e.g.*, nitrogen, phosphorus) whose valency can be expressed by odd numbers alone (1, 3, 5) are called *Perissads*; and elements (*e.g.*, sulphur, carbon) whose valency can be represented by even numbers alone are called *Artiads*.

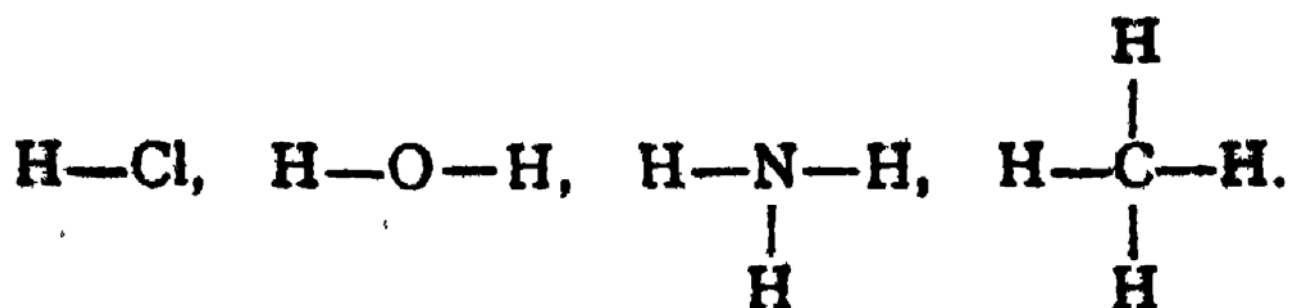
Saturated and Unsaturated Compounds.—When an element exerts its full valency, its chemical affinities are said to be *satisfied*, and the resulting compound is called *Saturated*. On the other hand, a compound in which one of the constituent elements has its affinities still unsatisfied, is called *Unsaturated*. For example, carbon being a tetrad element, CH_4 and CO_2 are saturated compounds, while C_2H_2 and CO are unsaturated compounds. In the case of an unsaturated compound the unsatisfied combining power of the element concerned, is not destroyed, but remains dormant or latent. This latent power becomes active under suitable conditions, and the unsaturated compound becomes saturated, as when CO unites with 2 more atoms of oxygen to form CO_2 .

Graphic Notation of Valency.—Valencies are represented graphically, *for illustrative purposes*, by lines or dashes affixed to the symbols of elements—each line signifying the power of combining with a monovalent atom. These lines are called *bonds* or *affinities*. Thus a monad is represented as having one affinity, a dyad as having two affinities, and so on:

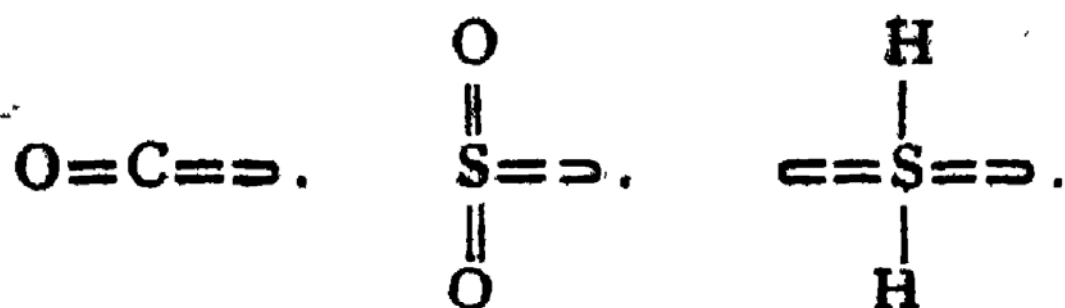


In the case of a compound, the lines are appropriately placed so as to serve as links between the combining elements.

For example, the compounds HCl , H_2O , NH_3 , CH_4 may be respectively represented by the following graphic formulæ:



In the case of an unsaturated compound, the unsatisfied affinities are represented as grasping each other so as to neutralise their powers. Thus, CO , SO_2 , and SH_2 may be graphically represented as follows:



NOTE.—The lines in the graphic notation do not imply the real arrangement of atoms or constitution of molecules. The length and direction of the lines are also immaterial.

Compound Radicals.—A *radical* (or *radicle*) means an unsaturated element or group of elements. Atoms of different elements sometimes hold together, forming definite groups which enter into the composition of more than one compound and pass unchanged (*i.e.* without decomposition) from one compound into another. These groups of atoms behave like single atoms of elements, and are called *Compound Radicals*. Such is the group NH_4 which occurs in a series of compounds— NH_4OH , NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{SO}_4$. Other examples of compound radicals are OH , CN , CO_3 , NO_3 , SO , &c.

A compound radical appears as an unsaturated compound, and its valency is measured by the degree of its unsaturation. Thus, the compound radical OH , in which one affinity of oxygen is unsatisfied, is monovalent. Similarly, NO_3 is monovalent, CO_3 is divalent, PO_4 is trivalent, and so forth.

University Examination Questions.

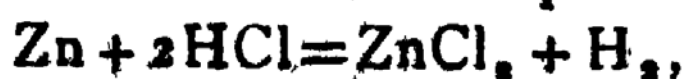
1. What is meant by the valency of an element? [A. 94, 01].
What do you understand by the *valency* of elements? How is it measured? Arrange the following elements according to their valency:—Carbon, nitrogen, chlorine, calcium, mercury. Give graphic formulæ of one compound of each in which the valency is fully satisfied [C. 1916].
2. What do you understand by *univalent*, *bivalent* and *trivalent* elements? [C. 93]. Give examples of univalent, bivalent and trivalent elements [A. 94]. Arrange the non-metallic elements in groups according to their valency [A. 97].
3. What relation exists between the following in the case of gases:—atomic weight, molecular weight, equivalent weight, valency, vapour density, and volume? [A. 06].
4. Write down in columns the atomic weight, equivalent, and valency of chlorine, phosphorus, sulphur, carbon, and calcium [A. 01].
5. Explain what is meant by a valency of (1) Phosphorus, (2) Copper, (3) Sulphur, (4) Silicon, (5) Nitrogen. How may the valency of one and the same element vary? What is the *effective* valency of Nitrogen in Ammonia, of Sulphur in Sulphur dioxide gas, and of Phosphorus in Phosphorous and Phosphoric chloride? [A. 09].
6. Explain the term 'Compound radicles.' [A. 1914].

CHAPTER XII.

CHEMICAL EQUATIONS AND CALCULATIONS.

Chemical Equations.—A chemical equation is the symbolic expression of a chemical change. The symbols and formulæ of the reacting substances in their required proportions, form the left-hand side of the equation: when there are two or more reacting substances (as is generally the case), their formulæ are connected by the sign + (*plus*). Similarly, the symbols and formulæ of the resulting substances are joined by the sign +, and form the right-hand side of the equation.

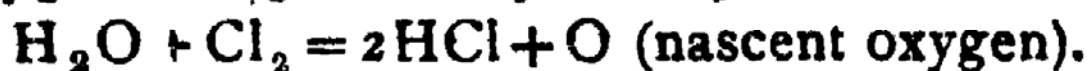
The sign of equality ($=$) is placed between the two sides, showing that the total number of atoms on the two sides of the equation is the same (in other words, that matter is indestructible). On the left-hand side the sign $+$ implies 'chemical combination'; whereas, on the right-hand side it bears the simple algebraic meaning; the sign $=$ means 'produce.' Thus, when we have the equation



we mean that one molecule of zinc combines with two molecules of hydrochloric acid to produce one molecule of zinc chloride and one molecule of hydrogen.

It should be observed that in chemical equations substances are always represented in complete molecules. Thus, in order to express the action of heat on red oxide of mercury, we must have the equation $2\text{HgO} = 2\text{Hg} + \text{O}_2$, and not $\text{HgO} = \text{Hg} + \text{O}$; because, O means an atom of oxygen which is incapable of separate existence.

Nascent State of Elements.—An element at the moment of its liberation from a compound is said to be in the *nascent state*. In this atomic condition the element is more active than when its atoms have united together to form molecules. For example, ordinary oxygen does not destroy vegetable colours; but when water is decomposed by chlorine, the nascent oxygen attacks colouring matters. The atomic state of oxygen is expressed by the equation—

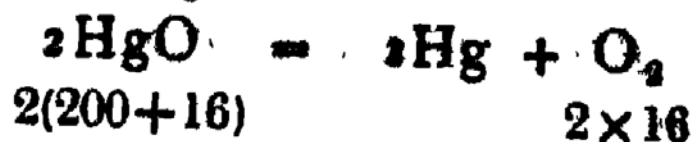


Chemical Calculations.—Calculations in Chemistry, as in other branches of physical science, are generally made according to the Metric System of weights and measures. Chemical problems involve calculations of weight only, or of volume only, or of both weight and volume.

Calculations relating to Weight.—In calculations relating to the weights of substances that take part in a chemical change, it is convenient first to write out the equation and then to note under each formula the weights of the substances concerned.

EXAMPLE 1. *To find the weight of oxygen given off by heating 100 grams of mercuric oxide.*

The following is the equation

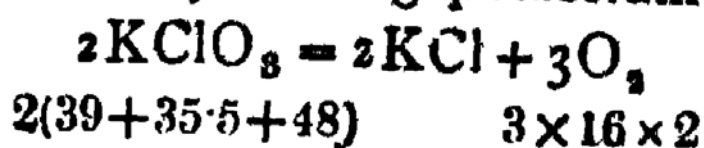


Here we find 2×216 parts of HgO yield 2×16 parts of oxygen. We are to calculate what weight of oxygen will 100 grams of HgO produce :

$$216 : 100 :: 16 : x. \quad \therefore x = \frac{100 \times 16}{216} = 7.4 \text{ grams.}$$

EXAMPLE 2. *To find the weight of oxygen that can be obtained from 100 ounces of potassium chlorate.*

Oxygen is obtained by heating potassium chlorate—

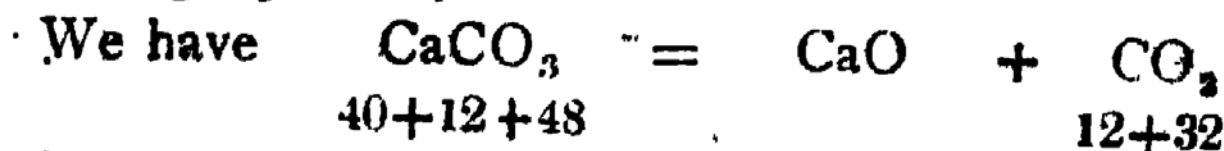


That is, 245 parts of KClO₃ produce 96 parts of oxygen ;

\therefore 100 ounces „ „ „ „ x ounces „ „

$$\text{where } x = \frac{100 \times 96}{245} = 39.18 \text{ ounces.}$$

EXAMPLE 3. *To find the weight of carbon dioxide evolved by heating 25 lbs. of chalk.*

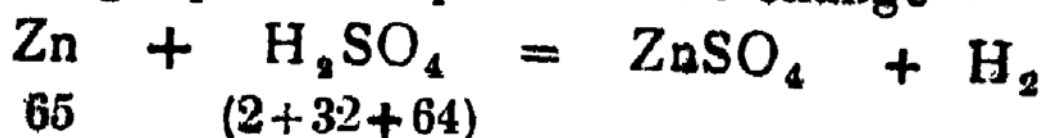


That is, 100 parts of chalk yield 44 parts of CO₂

\therefore 25 lbs. „ „ „ „ 11 lbs. „ „

EXAMPLE 4. *To find how much zinc can be dissolved in 100 grams of sulphuric acid.*

The following equation represents the change—



That is, 98 parts of H₂SO₄ dissolve 65 parts of zinc :

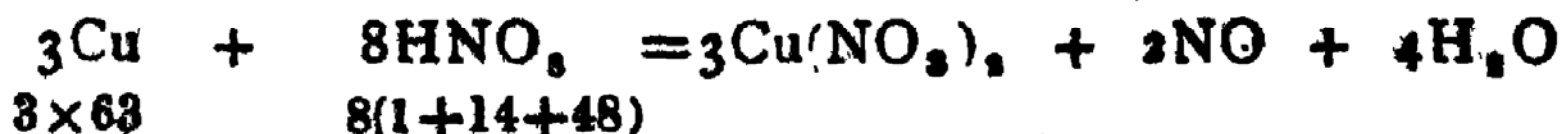
\therefore 100 grams „ „ „ „ x grams „ „

$$\text{where } x = \frac{100 \times 65}{98} = 66.326 \text{ grams.}$$

EXAMPLE 5. *To find how much nitre is required to produce sufficient nitric acid that can dissolve 100 grams of copper.*

Here we have to perform two calculations—(1) to find the weight of nitric acid required to dissolve 100 grams of copper, and (2) to find the weight of nitre necessary to produce the required weight of nitric acid :

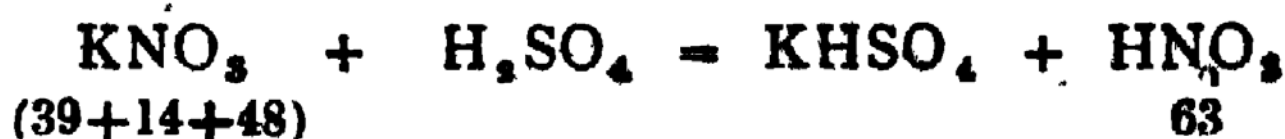
First we have—



That is, 3×63 parts of copper require 8×63 parts of HNO_3

$$\therefore 100 \text{ grams} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{8 \times 100}{3} \text{ grams} \quad \text{,,} \quad \text{,,}$$

Next we have—



That is, 63 parts of HNO_3 require 101 parts of KNO_3

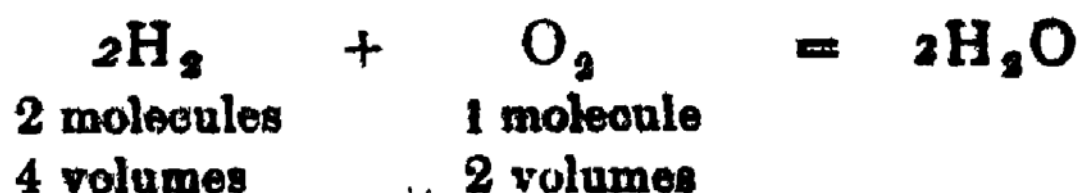
$$\therefore \frac{8 \times 100}{3} \text{ grams} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad x \text{ grams} \quad \text{,,} \quad \text{,,}$$

$$\text{where } x = \frac{8 \times 100 \times 101}{3 \times 63} = 427.5 \text{ grams nearly.}$$

Calculations of Volumes.—We have sometimes to calculate only the volumes of gases taking part in a chemical change, without any consideration of their weights. We have learnt from Avogadro's Law that molecules of all true gases occupy the same space, and that a molecule of a gas is represented as occupying two volumes. The volume may be expressed in litres, or cubic feet, or pints, &c.

EXAMPLE 1. *To find the volume of oxygen required for the combustion of 200 c.c. of hydrogen.*

The combustion of hydrogen in oxygen is thus represented—

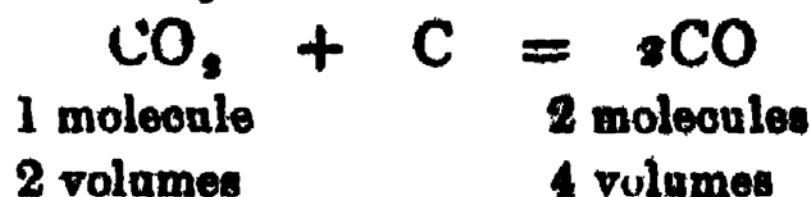


That is, 4 volumes of hydrogen require 2 volumes of oxygen

$$\therefore 200 \text{ c.c.} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad 100 \text{ c.c.} \quad \text{,,} \quad \text{,,}$$

EXAMPLE 2. *To find how many pints of gas are produced by passing 100 pints of carbon dioxide over red-hot charcoal.*

The reaction is represented thus—



That is, 2 volumes of CO_2 produce 4 volumes of CO

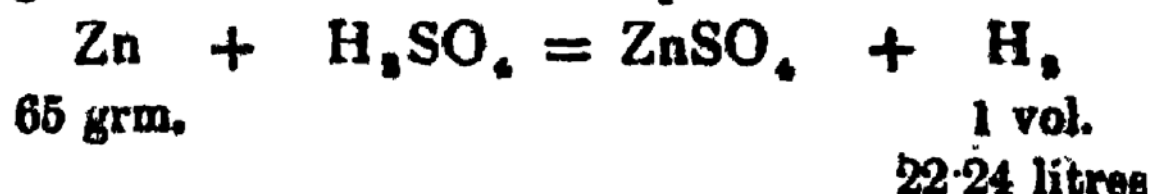
\therefore 100 pints " " " 200 pints " "

Calculations of Volumes from Weights.—In calculating the volume occupied by a given weight of a gas, we must know either the weight of a litre of hydrogen or the volume occupied by a gram of hydrogen. It has been found by experiments that the weight of one litre of hydrogen at NTP is 0.0899 gram (this quantity being called the *crith*). Hence, by simple Rule of Three, 2 grams of hydrogen at NTP occupy 22.24 litres.

The weights of gases being proportional to their densities, it follows that 22.24 litres of oxygen weigh $16 \times 2 = 32$ grams, that 22.24 litres of carbon dioxide weigh $44 \times 2 = 88$ grams, and so on. Now, twice the density is equal to the molecular weight. Hence, *the molecular weight (in grams) of any gas occupies 22.24 litres.*

EXAMPLE 1. *To find how many litres of hydrogen are evolved by the action of sulphuric acid on 100 grams of zinc.*

Putting the atomic weight (in grams) of zinc and the volume of hydrogen evolved, under the equation, we have—



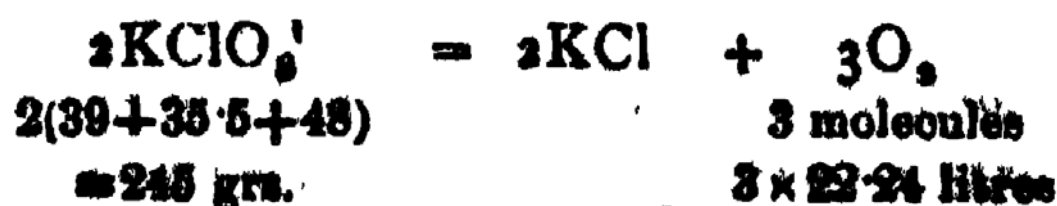
That is, 65 grams of zinc evolve 22.24 litres of hydrogen

\therefore 100 " " " " x " " "

$$\text{where } x = \frac{100 \times 22.24}{65} = 34.2 \text{ litres.}$$

EXAMPLE 2. *To find the volume of oxygen obtained by heating 100 grams of potassium chlorate.*

Here we have—



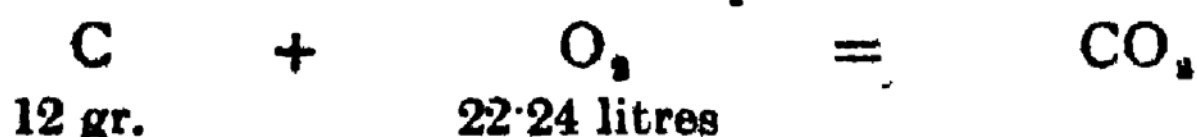
That is, 245 grams of KClO_3 yield 3×22.24 litres of oxygen

\therefore 100 " " " " x " " "

$$\text{where } x = \frac{100 \times 3 \times 22.24}{245} = 27.23 \text{ litres.}$$

EXAMPLE 3. *To find the volume of oxygen required for the combustion of 10 grams of carbon, at 15°C . and 744 mm.*

The combustion of carbon is represented thus—



That is, 12 grams of carbon require 22.24 litres of oxygen

\therefore 10 " " " " x " " "

$$\text{where } x = \frac{10 \times 22.24}{12} = 18.6 \text{ litres.}$$

Now 18.6 litres is the volume of oxygen required at NTP. We are now to correct this volume for 15°C . and 744 mm.

pressure. Using the combined formula $V = \frac{V' P' T}{P T'}$, we have

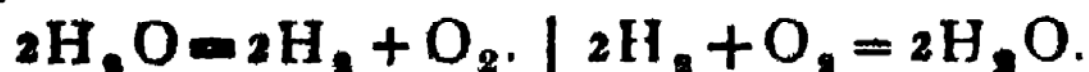
$$\text{required volume} = \frac{18.6 \times 760 \times (273 + 15)}{744 \times (273 + 0)} = 20 \text{ litres nearly.}$$

Examination Questions on chemical calculations will be found below the respective chapters in Parts II & III.

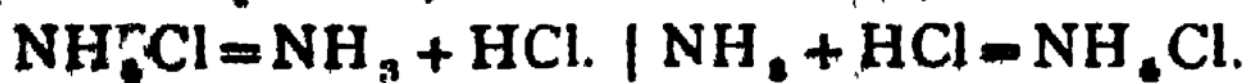
CHAPTER XIII.

DISSOCIATION AND ELECTROLYSIS.

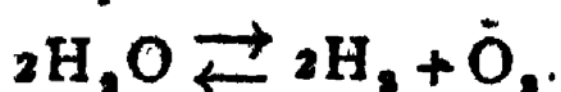
Dissociation.—This term implies a special kind of decomposition, in which a compound breaks up by the action of heat into simpler substances which unite again when cooled. For example, when we strongly heat steam, it is dissociated into hydrogen and oxygen; but these combine again at a lower temperature—



Similarly, when ammonium chloride is heated it splits up into ammonia and hydrochloric acid, but the products reunite when cooled (*vide* Chap. XXI, Ammonium Salts)—



Changes like the above are called *reversible* or *balanced actions*, and are thus represented—



It should be noted that all chemical actions are not so reversible. For example, when potassium chlorate is decomposed, the products do not reunite under any circumstances.

Electrolysis.—When an electric current is passed through different substances, we find that some allow the current to pass, while others resist the passage of electricity. The former are called *conductors*, and the latter *non-conductors*. Conductors are of two kinds: (1) some are merely physically changed by a current of electricity, such are the metals and a few non-metals; (2) others are decomposed when an electric current passes through them or their solutions, such are the salts, alkalies and strong acids (HCl, &c). The process of decomposing liquids by passing through them an electric current, is called *Electrolysis*. The liquid which is thus decomposed is called an *Electrolyte*. The plate of metal or end of wire which leads the electric current into the electrolyte, is called the *positive electrode* or *anode*: and that leading the current from the electrolyte, is called the *negative electrode* or *cathode*.

Subjecting various compounds to electrolysis, we find that, as results of their decomposition, *hydrogen and the metals appear at the negative electrode, while oxygen and other non-metals appear at the positive electrode*. The products of electrolysis sometimes interact with the electrolyte or solvent. Thus when we electrolyse an aqueous solution of sodium chloride, chlorine appears at the positive electrode: but sodium which would have appeared at the negative electrode interact with water, producing caustic soda and hydrogen which appear at the negative electrode. [$2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$].

The Ionic Theory.—The phenomena of electrolysis are now explained by what is known as the Ionic Theory

or the theory of 'Electrolytic Dissociation'. This theory supposes that electrolytes contain the elements mostly in a dissociated condition, *i. e.* as separated atoms. These disunited atoms are called *ions*, and are charged either with positive or with negative electricity. When an electrolyte is under the influence of an electric current the positive and negative ions carry their respective charges to the opposite electrodes, where they give up their charges and unite to form molecules. Metals and hydrogen which carry positive electricity and are thus attracted by the negative electrode or cathode, are called *electro-negative* or *cations*; the non-metals which convey negative electricity to the positive electrode or anode are called *electro-positive* or *anions*.

University Examination Questions.

1. Write a short account of the phenomenon termed 'dissociation'. Which of the following substances 'dissociate' when heated :— (a) Ammonium nitrate, (b) ammonium chloride, (c) Calcium carbonate, and (d) potassium chlorate? Give reasons for your answer. [A. 1914]. Explain the term Dissociation [C. 1915].
2. Define Electrolysis. [A. 04].
3. Write a short note on the Ionic Theory. [A. 1915].

CHAPTER XIV.

CLASSIFICATION OF ELEMENTS.

Metals and Non-metals.—Elements are commonly divided into two classes, *viz.*, Metals and Non-metals. Gold, copper, iron, mercury, &c. are metals; while, oxygen, chlorine, sulphur, phosphorus, &c. are examples of non-metals. The physical characteristics of metals are :— they are opaque bodies, and many of them are ductile and malleable; they can conduct heat and electricity, and possess metallic lustre (*i. e.* their polished surfaces reflect light): these properties are more or less absent from non-metals. Taking the chemical differences into consideration, the two classes may be broadly defined thus :— *Metals are electro-positive elements and their oxides*

usually form bases, while Non-metals are electro-negative elements and their oxides form acids. [See chapter on Metals].

Strictly speaking, there is no real distinction between the two classes, and in some cases it is difficult to decide whether an element should be called a metal or a non-metal. For example, arsenic possesses many physical properties peculiar to metals, but in its chemical properties it resembles non-metals. Elements (like arsenic) whose properties are intermediate between those of a metal and of a non-metal, are called *Metalloids*.

The Periodic Law.—It was long believed that there was a certain relation between the properties of elements and their atomic weights. In 1864 Newlands laid down the *Law of Octaves* in which he pointed out that 'if the elements were arranged in the numerical order of their atomic weights, there was a recurrence of similar chemical and physical characters at every eighth element'. This law was, in 1869, developed by Mendelejeff into what is known as the *Periodic Law* which is thus stated :—*The properties of elements (as well as of their compounds) are periodic functions of their atomic weights.* In accordance with this law Mendelejeff formulated a table of classification of all elements, and this Periodic System is now regarded as the most natural or scientific scheme of classifying elements.

The meaning of the Periodic Law will be clear from the following tabular arrangement of some of the elements which are arranged in the order of their atomic weights in four rows of seven each :

Series	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII
1	Li (7)	Be (9)	B (11)	C (12)	N (14)	O (16)	F (19)
2	Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
3	K (39)	Ca (40)	Sc (44)	Ti (48)	V (51)	Cr (52)	Mn (55)
4	Cu (63)	Zn (65)	Ga (70)	Ge (72)	As (75)	Se (79)	Br (80)

On looking into the table we find—

(1) The members of every series exhibit a regular gradation in their properties. Thus, lithium is univalent, beryllium is divalent, boron is trivalent, carbon is quadrivalent, and so on. This gradation is also seen in the power of the elements of a series to form compounds with oxygen.

(2) The members of every group exhibit a regular resemblance. Thus, lithium, sodium, and potassium are all univalent metals which decompose cold water and form alkalies. Similarly, there is a close resemblance between carbon and silicon, between fluorine, chlorine, and bromine.

Hence we have the law that *when elements are arranged in the order of their atomic weights there appear a gradation and resemblance of their properties at regular periods or intervals*. The Periodic Law has been of great service in detecting the atomic weights of elements; it has also led on to the discovery of new elements, and suggested new lines of research.

Allotropy.—Certain elements exist in more than one form, the several forms having different characteristics. For example, the same element carbon has the different varieties—diamond, graphite, and charcoal. This property of some elements to assume different forms is called *Allotropy* or *Allotropism*. The less known varieties are called the *Allotropes* or *Allotropic modifications* of the more common form. Thus, ozone is called an allotrope of oxygen. Allotropy is believed to be due to differences in the constitution of the molecules of an element. [See under Ozone, Carbon, Sulphur, Phosphorus].

University Examination Questions

1. State the chief points of chemical difference between metals and non-metals [A. 03]. What do you understand by *metallic* and *non-metallic* elements [C. 93].

2. Why are the elements classed in families? Give full reasons and illustrations in your answer [A. 95].

3. What is Allotropy (or Allotropism)? [C. 94, 1900, 02, 06, 09, 1911; A. 94, 96, 98, 04, 07, 15]. Certain elements are capable of

existing in allotropic modifications. Explain and illustrate this statement [C. 97].

Mention as many sets of allotropic substances as you remember [A. 07]. Describe the allotropic forms of carbon, phosphorus and oxygen [A. 94, 98]. To what may the allotropism be due? [A. 94].

CHAPTER XV.

ACIDS, BASES, AND SALTS: NOMENCLATURE.

Acids, Bases, and Salts.—The following simple experimental facts will be of help in understanding what are called acids, bases, and salts:

If we burn in gas-jars fragments of carbon, sulphur, phosphorus, sodium, potassium, and magnesium, and then shake up with water the oxide produced in each case, we shall find that two classes of substances have been formed. The solutions of the oxides of the non-metals (carbon, sulphur, and phosphorus) will have sour taste and will turn blue litmus red: these solutions are called *acids*, and the oxides from which they are formed are called *acidic oxides* or *anhydrides*. On the other hand, the solutions of the oxides of the metals (sodium, potassium, and magnesium) will have soapy taste and will turn red litmus blue: these are called *bases*, and the oxides producing them are called *basic oxides*.

Next, if we try the action of a base on an acid, a substance may be produced that will behave neither like an acid nor like a base; it will be neutral. In this case the acid and the base are said to *neutralise* each other, and the resulting substance is called a *salt*. For example, the action of the base potassium hydroxide (KOH) on the common acids is to produce a salt and water in each case—



From similar other experiments we learn that

(1) *An acid contains hydrogen (and can turn blue litmus red):*

- (2) *A base contains a metal (and can turn red litmus blue) :*
- (3) *An acid and a base act upon each other—the hydrogen of the acid exchanging place with the metal of the base—with the result that :*
- (4) *A salt is produced from the acid by the replacement of its hydrogen by a metal, and*
- (5) *Water is produced from the base by the replacement of its metal by hydrogen.*

Neutralisation.—This word means mutual destruction of individual properties. It is specially used to denote the action of an acid and a base upon each other. When an acid and a base are brought together in proper proportions the characteristic properties of both the substances are destroyed. They are then said to neutralise each other, salt and water being produced at the same time. [See Chap. XVI].

Acids.—An Acid is a compound substance containing hydrogen, which hydrogen may be entirely or partially replaced by a metal (or a compound positive radical, *i.e.* a group of elements behaving like a metal). The result of displacement of the hydrogen of an acid by a metal is the production of a salt. Most acids have a sour taste, and change the colour of blue litmus to red.

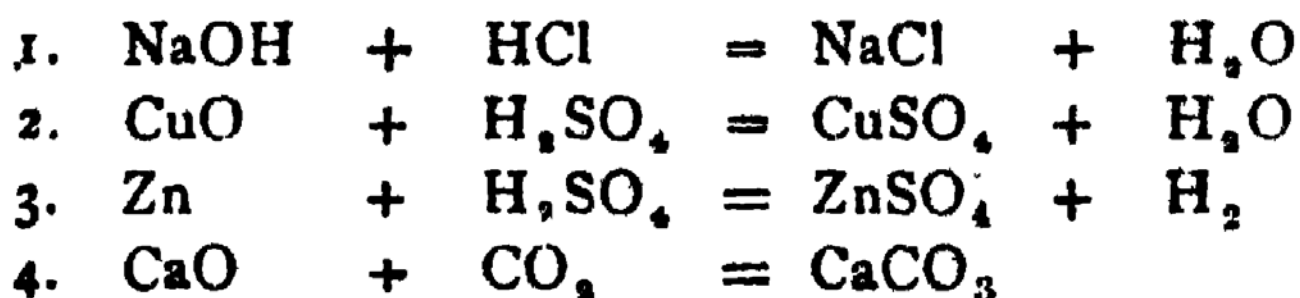
All acids contain hydrogen, and many contain also oxygen. Those acids in which oxygen is present are called *oxy-acids*, such as is sulphuric acid (H_2SO_4); those acids in which oxygen is absent are called *hydracids*, such as is hydrochloric acid (HCl).

NOTE.—It was formerly believed that all acids (and all bases) contained oxygen; but this 'oxygen theory' has been discarded in view of the fact that some substances (as HCl , HCN) which are undoubtedly acids do not contain oxygen. The modern theory is that all acids must contain hydrogen. But it should not be supposed that all substances which contain hydrogen are acids.

Bases.—A base is a compound substance containing oxygen, hydrogen, and a metal (or a compound positive radical), which metal can replace the hydrogen of an acid to form a salt.

Bases are commonly called *hydroxides* or *hydrates*,* and basic oxides are also sometimes called bases. The more active bases that are soluble in water are called *alkalies*: they have caustic properties, and turn red litmus blue as also yellow turmeric paper brown; such are caustic soda or sodium hydroxide (NaOH) and caustic potash or potassium hydroxide (KOH). Other bases are not much soluble and have not the strong properties of alkalies; such are slaked lime or calcium hydroxide (CaH_2O_2), barium hydroxide (BaH_2O_2), &c. There are even bases which have very little action on litmus; such is ferric hydrate, $\text{Fe}_2(\text{HO})_3$. An aqueous solution of ammonia (NH_4OH) behaves like a base.

Salts.—A salt is a compound substance derived from an acid by wholly or partially replacing its hydrogen with a metal or a compound positive radical. Salts may sometimes be formed by the direct union of a metal with a non-metal; thus we have, $2\text{Na} + \text{Cl}_2 = 2\text{NaCl}$. But they are* usually produced by the action of an acid on (1) a base or (2) a basic oxide or (3) a metal, or (4) by the action of an acidic oxide on a basic oxide. Thus—



Salts usually possess a saline taste and are neutral to litmus. Litmus itself is a salt of a vegetable acid.

Precipitation.—It is the chemical process by which a substance is made to separate from others in a solution, and to fall to the bottom of the containing vessel. When solutions of two salts are mixed together and by their double decomposition an insoluble salt is produced, then the insoluble salt separates from the solution in the solid state, and is then called a *Precipitate*.

* These words are, however, no longer regarded as synonymous. *Hydrate* is used as a general term for 'solids containing water', and the hydrates of basic oxides only are called *hydroxides*.

For example, we obtain a precipitate of calcium carbonate by adding a solution of sodium carbonate to a solution of calcium chloride. Similarly, silver chloride is precipitated by mixing solutions of silver nitrate and sodium chloride—



Basicity of Acids : Normal, Acid, and Basic Salts.—

The *basicity* of an acid means its power of combining with a base, and is measured by the number of replaceable hydrogen atoms contained in the acid. When the acid contains only one atom of hydrogen that can be replaced by a metal, the acid is called *monobasic*: such is nitric acid (HNO_3). Acids containing two or three replaceable hydrogen atoms are called *dibasic* and *tribasic*; such are sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) respectively.

When all the replaceable hydrogen of an acid is displaced by a metal the resultant salt is called a *neutral* or *normal salt*. But sometimes a salt is formed by a partial displacement of the hydrogen of a dibasic or tribasic acid; such a salt still retains some of the properties of the acid, and is called an *acid salt*. Thus, of the two salts Na_2SO_4 and NaHSO_4 formed from sulphuric acid (H_2SO_4), the former is called 'normal sodium sulphate', and the latter called 'acid sodium sulphate.'

There are some salts produced from oxyacids by union of a larger proportion of a base than is necessary for the production of the normal salt: such salts are called *basic salts*. For example, normal lead carbonate has the composition PbCO_3 , but what is known as 'white lead' is a basic lead carbonate [$(\text{PbCO}_3)_2, \text{PbH}_2\text{O}_3$].

Chemical Nomenclature.—There is no strict nomenclature in Chemistry, although it is the attempt of modern science to name substances according to a scientific system. The names of the elements have been formed in various ways; but as a rule the names of metals end in *-um*. Thus, familiar metals like gold, silver, copper, &c. are called by their Latin

names *aurum*, *argentum*, *cuprum*, &c. Selenium and tellurium, however, are non-metals.

Of Binary Compounds.—Substances consisting of two elements are called *Binary Compounds*, and those composed of three elements are called *Ternary Compounds*. The following are the rules of naming binary compounds:—

(I) The names of binary compounds are formed of the names of the constituent elements; and as most of them are made up of a metal and a non-metal, the name of the metal is placed first and the termination *-ide* is added to the name of the non-metal. Thus, we have 'copper oxide', 'sodium chloride', 'lead sulphide', and so forth.

(II) When there are more than one compound of the same two elements, the compounds are distinguished from each other either (1) by the numerical prefixes *mono-*, *di-*, *tri-*, &c, or (2) by the suffixes *-ic* and *-ous*, the termination *-ic* implying greater proportion of oxygen (or other non-metal) and *-ous* implying less proportion of it. Thus, we have nitrogen monoxide (or nitrous oxide), nitrogen dioxide (or nitric oxide), nitrogen trioxide, &c.

Common substances are more often called by their familiar names than by their chemical names. Such are water (hydrogen monoxide), common salt (sodium chloride), ammonia (hydrogen nitride), sulphuretted hydrogen (hydrogen sulphide), hydrochloric acid (hydrogen chloride), &c.

Of higher compounds (Acids and Salts).—Ternary and higher compounds are also named after the names of their principal constituent elements, according to methods similar to those applied in the cases of binary compounds. Sometimes in naming a group of acids the prefixes *per* (=over) and *hypo* (=under) have to be used, to denote a still higher or lower proportion of oxygen than what has already been denoted by the terminations *-ic* and *-ous* respectively. Thus we have the ascending series hypochlorous acid (HClO), chlorous acid (HClO_2), chloric acid (HClO_3), and perchloric acid (HClO_4).

Salts are named after the acids from which they are formed: the terminations *-ite* being applied to the salts of those acids that have the suffix *-ous*, and the termination *-ate* to the salts of those acids that have the suffix *-ic*. For example, sulphurous acid produces sodium sulphite, and sulphuric acid produces sodium sulphate; potassium nitrite is formed from nitrous acid, and potassium nitrate from nitric acid.

University Examination Questions.

1. Define the terms— acid, alkali, base, salt, neutralisation illustrating your definition in each case by an example [C.98,04; A. 1911]. Define basic oxide, acid-forming oxide, base, acid, and salt, and give examples [C.06]. What are the characteristic properties of *acids*, *bases*, and *salts*? Give examples of each [C. 1912.]

2. What is meant by the basicity of an acid? State the basicity of nitric acid, sulphuric acid, and (ortho)phosphoric acid, giving reasons for your statements. Define the terms normal salt, acid salt, and basic salt giving examples of each class [C.01; A. 1911, 13]. Explain the following terms:—monobasic and dibasic acids, acid and normal salts [A. 93,95]. Explain the terms Monobasic, Dibasic, and Tribasic acids; illustrate your reply by examples and give the formulæ of the salts which these acids may form with sodium and potassium [C.95; A. 07].

If M is a monad element, and D a dyad one, give symbols of their chlorides, nitrates, sulphates and carbonates [A. 95].

CHAPTER XVI.

ACIDIMETRY AND ALKALIMETRY.

Acidimetry and Alkalimetry.—Acidimetry (or Acetimetry) and Alkalimetry are the chief methods used in Volumetric Analysis, and mean respectively the methods of determining the strength of an acid or alkali, *i. e.* the amount of real acid or alkali present in a substance. The methods consist in adding, to a measured volume of a substance, an acid or alkali solution of known strength, until the substance is exactly neutralised. The volume of the standard solution used determines the strength of the substance under examination.

Their Requisites.—For acidimetric and alkalimetric purposes the following things are required :

(i) *Apparatus* :—Chemical balance, measuring cylinders or flasks, pipettes, and burettes. See pp. 15, *sq.*

(ii) *Indicators* :—These are substances which indicate by their change of colour whether a liquid is acid, alkaline, or neutral. The following are the indicators—

1. **TURNBULL'S** : it is pale yellow with acids, and reddish brown with alkalies.

2. **LITMUS** : it turns red with acids, and blue with alkalies. [Litmus fails when used with alkaline carbonates and should not be used when working by gas-light].

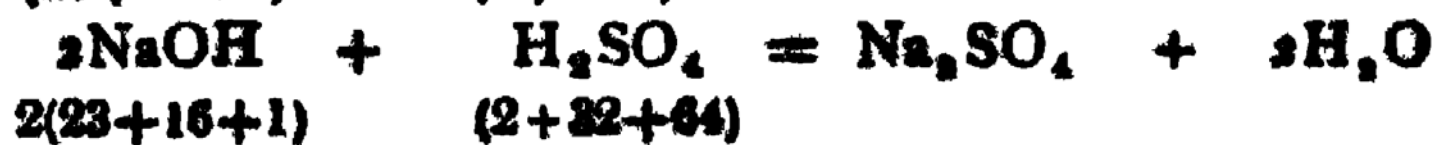
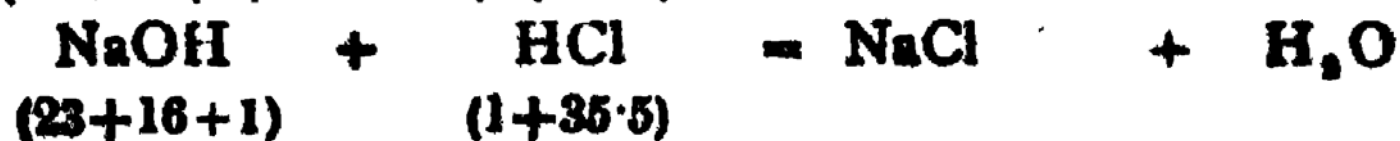
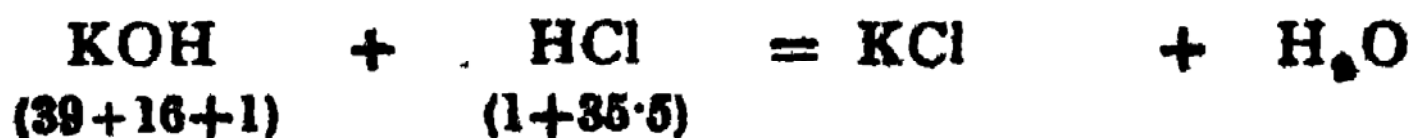
3. **PHENOL-PHTHALEIN** : it remains colourless with acids, but turns pink (magenta red) with alkalies. [It is more sensitive than litmus and is suitable when a weak acid is to be titrated. It should not be used with ammonia].

4. **METHYL-ORANGE** : it is pink or red with acids, and yellow with alkalies. [Unlike litmus, it is not affected by carbonic acid, but cannot be used with oxalic and other organic acids. It is specially useful when a weak base is to be titrated].

5. **COCHINEAL** : it is yellow with acids, and reddish violet with alkalies. [It is unaffected by carbonic acid, and is particularly useful when working by artificial light].

(iii) *Standard Solution* :—It is a solution of known strength *i. e.*, a solution which contains in a known volume of it a known weight of a substance. A standard solution can be prepared of any strength ; but a 'normal' solution is what is generally used.

Normal and Decinormal Solutions.—To understand what is meant by a normal solution, let us consider the following reactions—



We find that 56 parts of KOH and 40 parts of NaOH neutralise the same weight (36.5 parts) of HCl. Hence, if we separately dissolve 56 grams of KOH and 40 grams of NaOH in one litre of water, we obtain two alkaline solutions which have equal neutralising power. These two solutions are called *normal alkaline solutions*.

Again, we find that 36.5 parts of HCl neutralise 40 parts of NaOH, and that 98 parts of H_2SO_4 neutralise 80 parts of NaOH. That is, 36.5 parts of HCl and $98 \div 2 = 49$ parts of H_2SO_4 neutralise the same weight of NaOH. Now, if we prepare two aqueous solutions, one containing 36.5 grams of HCl per litre and the other containing 49 grams of H_2SO_4 per litre, the two solutions will have equal neutralising power. The solutions in these cases are called *normal acid solutions*.

Hence we have the definition:—*A normal solution is one which contains per litre one equivalent weight in grams of an acid or an alkali.* In a normal acid solution there is in one litre of it one gram of the replaceable hydrogen, and in one litre of a normal alkali solution there is the equivalent weight (in grams) of the hydrogen-replacing metal. For example, a normal solution of nitric acid (HNO_3) contains $1 + 14 + 48 = 63$ grams of HNO_3 per litre, that of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) contains $\frac{1}{2}(2 + 24 + 64) = 45$ grams of $\text{H}_2\text{C}_2\text{O}_4$ per litre, that of calcium hydroxide (CaH_2O_2) contains $\frac{1}{2}(40 + 2 + 32) = 37$ grams of CaH_2O_2 per litre. It is clear that *equal volumes of any two normal solutions, one acid and the other alkaline, exactly neutralise each other.*

When a normal solution proves too strong, we use solutions having one-tenth or one-hundredth of its strength. These solutions are respectively called *decinormal* and *centinormal solutions*.

Normal, decinormal, and centinormal solutions are symbolically represented as $\frac{N}{1}$, $\frac{N}{10}$, and $\frac{N}{100}$ respectively. Thus, $\frac{N}{1} \text{H}_2\text{SO}_4$ means a normal solution of H_2SO_4 , $\frac{N}{10} \text{KOH}$ means a decinormal solution of KOH, and so on.

Preparation of Normal or other Standard Solutions.—There are several methods of standardising given solutions, *i. e.* preparing normal, decinormal, and other solutions of known strength from the given solutions. Two typical processes are given below.

Normal Solution of Sulphuric Acid.—Suppose we are given a sample of pure commercial sulphuric acid having the specific gravity 1.84. From the Table* we find that this acid contains 95.6 per cent. of real H_2SO_4 , *i. e.* 100 grams of the acid contain 95.6 grams of H_2SO_4 . And, as the volume of 1.84 grams of the acid is 1 c.c., the volume of 100 grams is $\frac{100}{1.84}$ c.c.

Now, normal H_2SO_4 solution contains per litre 49 grams of H_2SO_4 . Let us calculate what volume of the commercial acid contains 49 grams of H_2SO_4 :

$$95.6 : 49 :: \frac{100}{1.84} : x. \quad \therefore x = \frac{49 \times 100}{95.6 \times 1.84} = 27.85 \text{ c.c. nearly.}$$

We have now to dilute 27.85 c.c. of the acid (or a definite portion of this volume) so that the solution may contain 49 grams of H_2SO_4 per litre (1000 c.c.). For this purpose we may measure off 13.925 c.c. (*i. e.* 14 c.c. nearly) of the acid, and pour it gradually into 200 c.c. of water; when the diluted acid has cooled, we must dilute it further to 500 c.c. We thus get 500 c.c. of a normal solution of H_2SO_4 . With this we can prepare 5 litres of decinormal solution.

Normal Solution of Sodium Hydroxide.—Suppose we are given a solution of NaOH of unknown strength and a normal solution of H_2SO_4 or any other acid. We take 20 c.c. of the NaOH solution, and add to it two drops of methyl-orange: the solution will be coloured yellow. We then gradually run from a burette the normal acid solution into the alkali solution, until the liquid is just coloured red.

* There are Tables and Curves which tell us the respective strengths of the chief acids and alkalies of varying specific gravities.

Suppose 22.5 c.c. of the normal acid were run in from the burette. Then 22.5 c.c. of the normal acid neutralise 20 c.c. of the given alkali solution. But 22.5 c.c. of the normal acid solution would exactly neutralise 22.5 c.c. of a normal alkali solution. Hence, in order to bring the given alkali solution to the normal standard, we must add to every 20 c.c. of it 2.5 c.c. of water. That is, 1 litre of the solution would require 125 c.c. more of water to give a normal solution.

Finding the Strength of an acid or alkali.—In order to determine the amount of an acid or alkali contained in a given substance we titrate it, *i.e.* measure its strength by means of a standard solution.

Titration.—It is the process of testing the strength of a solution by means of a standard solution. The process is the following:—A certain quantity of the given liquid (or solution of the given solid) is first measured off in a pipette or a measuring flask, and is placed in a flask or beaker. Some distilled water and an indicator are next added. The standard solution is then run in from a burette a little at a time until the indicator shows that a point of neutrality has been reached. The strength of the given substance is thus ascertained from the volume of the standard solution used.

EXAMPLE 1. *To find the strength of a solution of sodium hydroxide, using a normal acid solution.*

Let us take 25 c.c. of the NaOH solution and titrate by means of the normal acid solution. Suppose 30.5 c.c. of the acid solution are required for neutralisation.

Now, as the acid solution is of normal strength, whatever may be its nature (whether it be H_2SO_4 , or HCl , or HNO_3 , or $\text{H}_2\text{C}_2\text{O}_4$), 30.5 c.c. of it will neutralise 30.5 c.c. of normal NaOH solution. And as 1 litre of normal NaOH solution contains 40 grams of NaOH, 30.5 c.c. of it contain $\frac{30.5 \times 40}{1000} = 1.22$ grams of NaOH. That is, 25 c.c. of the given NaOH solution contain 1.22 gr. of NaOH. Therefore, 1000 c.c. of the given NaOH solution contain 48.8 grs. of NaOH.

N. B.—The strength of other alkalies may be ascertained by similar methods.

EXAMPLE 2. *To find the percentage of sodium carbonate in a sample of washing-soda.*

Let us weigh out exactly 4 grams of the washing-soda and dissolve it in water making up the solution to 100 c.c. Let us now take 25 c.c. of the solution (which will contain 1 gram of the washing-soda) and titrate by means of normal H_2SO_4 solution.

Suppose 6 c.c. of the normal acid are required for neutralisation. This would neutralise 6 c.c. of normal Na_2CO_3

solution, which contain $\frac{6 \times 53}{1000} = 0.318$ gram of Na_2CO_3 .

Hence, this 0.318 gram of Na_2CO_3 is also contained in 25 c.c. of the soda solution, *i.e.* 1 gram of the sample washing-soda. So, 100 grams of the washing-soda contain 31.8 grams of Na_2CO_3 , and the remaining 68.2 grams are water or other impurities.

NOTE 1.—The percentage of real sodium hydroxide in ordinary stick soda, or of potassium hydroxide in stick potash, may be determined by similar processes.

NOTE 2.—The strength or the percentage of a substance being known, we can easily prepare a normal solution of it. Thus in the above example,

31.8 gr of Na_2CO_3 are contained in 100 gr. of washing-soda
 $\therefore 53 \text{ " " " " " " } \frac{53 \times 100}{31.8} \text{ " " " " }$

We have now to dissolve this quantity of washing-soda in water, and by diluting make up the solution to 1 litre.

EXAMPLE 3. *To find the percentage of sulphuric acid in a sample of the commercial acid.*

Let us take a small quantity of the acid, and find its weight to be exactly 10 grams. Let us dilute the acid making up the solution to 100 c.c. We then take 20 c.c. of the solution (which contain 2 grams of the acid) and titrate with a normal alkali solution. Suppose 30 c.c. of the alkali solution are required.

Now, 30 c.c. of the normal alkali solution neutralise 30 c.c. of normal H_2SO_4 solution, which contain $\frac{30 \times 49}{1000} = 1.47$ grams

of H_2SO_4 . So, 1.47 grams of H_2SO_4 are contained in 2 grams of the sample acid; hence, 100 grams of the sample acid contain 73.5 grams of H_2SO_4 , the remaining 26.5 grams being impurities.

NOTE.—Normal solutions are used only for the sake of convenience. If instead we use any other standard solution, the result will be the same. Thus, suppose in the above experiment we use a solution containing 48 grams of NaOH per litre. Then we will find as a matter of fact that 25 c.c. of the alkaline solution will be required to neutralise 20 c.c. of the acid. Now, it may be easily seen that 25 c.c. of a solution containing 48 grams of NaOH per litre are equivalent to 30 c.c. of normal NaOH solution.

University Examination Questions.

1. Explain the term 'indicator' [C. 08].
2. How many grams of sodium hydrate are required to exactly neutralise 20 litres of hydrochloric acid gas at N.T.P.? [A. 03].
3. What weight of (a) sulphuric acid, and (b) hydrochloric acid will exactly neutralize 50 c.c. of a solution of anhydrous sodium carbonate which contains 50 grammes of this compound in a litre? ($\text{Na}=23$). [A. 05].
4. What *volume* of a ten per cent. solution of sodium carbonate will be required to neutralize a litre of a solution containing 4.9 grammes of sulphuric acid? [C. 1912]. What weight of sodium carbonate would be required to neutralize 50 c.c. of *normal* sulphuric acid? Describe how you would proceed to do it. [C. 1913].
5. 100 grams of hydrochloric acid solution of specific gravity 1.17 contain 33.4 grams of HCl. How many litres of acid solution of this strength would be required to neutralize 5 litres of a solution of sodium hydrate containing 0.042 gram of NaOH per cubic centimetre? [A. 1914].
6. In order to find the strength of a sample of hydrochloric acid, 10 grams were diluted with water and a piece of marble weighing 7 grams placed in it. When all action had ceased the marble was

removed, washed and dried, and was found to weigh 2.2 grams. What was the percentage strength of the acid? [A. 1911].

7. 7.0 grams of magnesium carbonate were added to double its weight of dilute sulphuric acid; after all action had ceased, it was found that 0.7 gram remained undissolved; calculate the percentage strength of the acid. [A. 1914].

8. 20 c.c. of a decinormal solution of nitric acid is neutralized by 22.5 c.c. of a solution of sodium carbonate. Calculate the strength of the carbonate solution in terms of normality and the weight of the carbonate per litre of the solution. In finding the point of neutralization, what indicator would you use, and why ($\text{Na} = 23$, $\text{C} = 12$, $\text{O} = 16$). [C. 1916].

PART II. NON-METALS.

CHAPTER XVII.

HYDROGEN.

ATOMIC WEIGHT 1. DENSITY 1. MOLECULAR FORMULA H_2 .

Occurrence.—Hydrogen occurs plentifully in nature ; but it is scarcely found in the free state, except when it is evolved with other gases during volcanic eruptions. It forms $\frac{1}{9}$ by weight of water, and is contained in all acids, organic bodies and mineral oils.

Preparation—The general methods of preparing the gas are (1) to displace it from a dilute acid by means of a metal, and (2) to decompose water. The gas is usually collected by displacement of water ; but it may also be collected by upward displacement of air.

1. *From diluted Acids.*—The acid usually employed is either sulphuric acid (H_2SO_4) or hydrochloric acid (HCl) *diluted with water*, the metal used being zinc, iron, magnesium, aluminium, or tin. Application of heat is not necessary for the reaction.

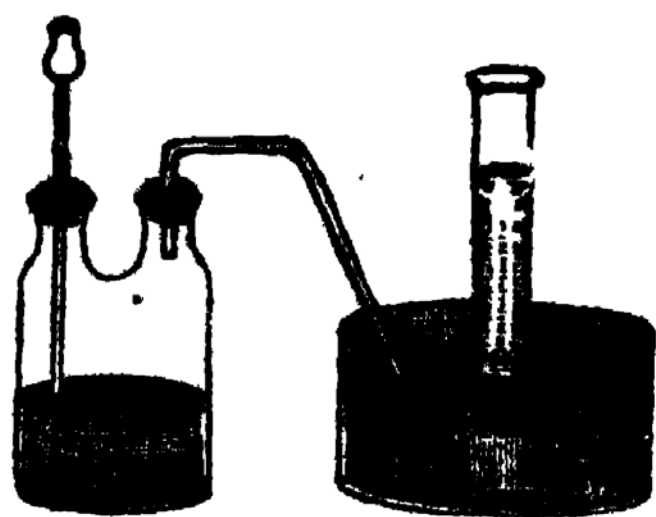
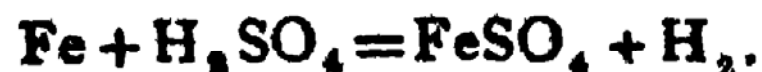
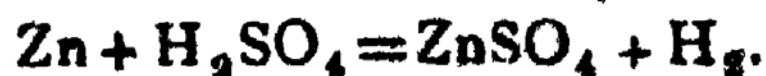


Fig. 23.

For laboratory purposes, granulated zinc is placed in a flask or woulf's two-necked bottle (Fig. 23) which is fitted up with a

thistle funnel and a delivery tube. On pouring the dilute acid down the funnel, a brisk evolution of the gas commences. After a few minutes (when the air in the bottle and tube has been expelled by the evolved gas),* it is collected over the pneumatic trough.



Fig. 24.

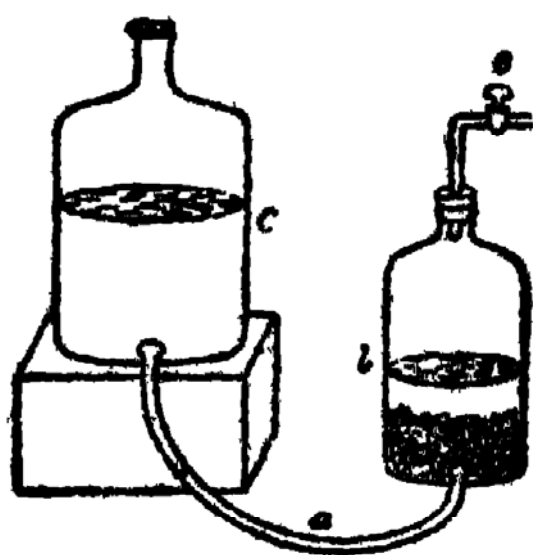


Fig. 25.

To obtain a ready supply of hydrogen, Kipp's apparatus (Fig. 24) or the apparatus shown in Fig. 25 is often used.

Granulated zinc is contained in *b*, and the diluted acid in *c* and *a*. On opening the stopcock *e*, the acid reaches the metal, and the gas is rapidly given off. When *e* is closed, the gas is still evolved, until its pressure

drives the acid away from the metal, so that the action ceases.

Purification.—In preparing hydrogen by the action of zinc on dilute sulphuric acid, commercial zinc is used, because pure zinc does not act with the acid. But as thus obtained the gas contains many impurities, *e.g.*, sulphuretted hydrogen, arseniuretted hydrogen, sulphur dioxide, oxides of nitrogen, and water vapour. These are got rid of by passing the gas through a series of U-tubes containing lead nitrate, silver sulphate, caustic potash, and phosphorus pentoxide.

II. From Water : (1) By the action of certain metals :

(a) *At ordinary temperatures* water is decomposed by the alkali metals (sodium, potassium, &c.) and the metals of the alkaline earths (calcium, strontium, and barium).

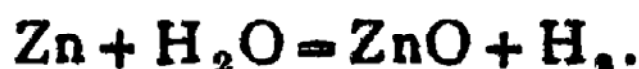
To illustrate the action, a small piece of sodium is wrapped in wire-gauze and plunged into water, over which is inverted a cylinder filled with water : hydrogen is at once evolved and

* This precaution is necessary in all experiments with hydrogen as well as other inflammable gases, because mixtures of the gases with air explode by contact with a flame.

collects in the cylinder. When potassium is used, the action is so vigorous that some of the potassium and the liberated hydrogen take fire.



(b) When *hot water* is acted upon by 'zinc-copper couple' (*i.e.*, zinc coated with copper), pure hydrogen is rapidly evolved. The zinc-copper couple (obtained by immersing granulated zinc in a dilute solution of copper sulphate) decomposes water even at ordinary temperatures : the zinc alone takes part in the reaction.

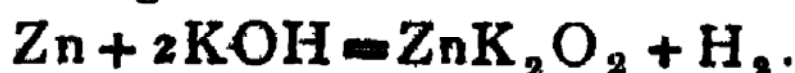


(c) When *steam* is passed over red-hot iron, magnesium, or zinc contained in a tube, hydrogen is liberated. For the *manufacture* of the gas, iron nails or filings are packed in an iron-tube which is strongly heated, and steam from a boiler is passed through it.



(2) By electrolysis.—See p. 9. $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$.

III. Hydrogen is also obtained by the action of zinc or aluminium on a boiling solution of caustic soda or potash.



Properties : Physical.—Hydrogen is a colourless, tasteless, inodorous, and non-poisonous gas. It diffuses very rapidly, as it is the *lightest substance* known. Hydrogen is therefore chosen as the standard for comparing the density of gases. [Its lightness is demonstrated by the ascent of soap bubbles filled with it, and by the fact that it can be poured upward. Thus, when a jar of hydrogen is held with its mouth below that of a jar of air, hydrogen and air exchange their places, *i.e.* hydrogen (which is much lighter than air) displaces air from the upper jar].

Chemical.—Hydrogen does not support combustion, but is an inflammable gas : it burns with a very pale blue flame which is very hot. Hence its old name 'inflammable air.' [If we push a lighted taper into an inverted jar of hydrogen, the hydrogen

will burn at the mouth of the jar, but the taper will be extinguished].

A mixture of hydrogen with oxygen or air (called 'detonating gas') explodes violently when it comes in contact with a flame or spark. Water is formed when hydrogen burns or explodes in air or oxygen: hence the name 'hydrogen,' i. e., water-producer. [If we light a jet of hydrogen and carefully hold over it a long open narrow glass tube (Fig. 6), a low musical note is heard: hence the name, 'the singing flame of hydrogen.' We see also a deposit of moisture on the sides of the tube, caused by the union of hydrogen with the oxygen of the air within the tube].



Hydrogen has great affinity for oxygen, and is thus a powerful reducing agent. [If we pass hydrogen over hot cupric oxide (CuO) or black oxide of iron (Fe₃O₄), hydrogen unites with oxygen and the metal is set free].



Tests.—(1) Hydrogen burns with a blue lambent flame, forming water.

(2) Limewater does not turn milky when poured into a vessel in which hydrogen has burnt.

University Examination Questions.

1. Describe three methods of preparing hydrogen and mention briefly its chemical and physical properties [C. 91]. How would you prepare pure hydrogen? What precautions would you take in the collection of the gas, and why? Mention the principal properties of the gas, and describe any two experiments that you have seen in the class in illustration of its properties [C. 08].

2. Describe a method for the preparation of hydrogen from (a) sulphuric acid, (b) iron and water [C. 02]. What happens when steam is passed through an iron tube filled with iron nails and heated to redness? [C. 98].

3. When sulphuric acid acts upon 1 gram of zinc, what volume of hydrogen will be liberated at 30° C. and 700 mm. pressure? [A. 04].

4. Calculate the weight of iron converted into oxide by the action of 18 grams of steam, and find the volume of hydrogen (measured at N. T. P.) produced in the same reaction [C. 04].

You are given a balloon with a capacity of a thousand litres and you wish to fill it with *hydrogen* at 30 C. and 750 mm. pressure. How much *iron* would you require for the purpose. Fe = 56. [C. 1912].

5. What volumes of hydrogen measured at 0°C. and 760 mm. pressure would be evolved on treating (a) 100 grammes of sodium with water, (b) 50 grammes of zinc with hydrochloric acid? The equivalent of zinc may be taken as 32.5 and that of sodium as 23. [C. 01].

6. One litre of hydrogen gas measured at 32°C and 758 m.m. pressure is burnt in excess of oxygen. What is the weight of water produced? [C. 07].

What volume of oxygen at 12°C and 780 m.m. will be required to burn all the hydrogen evolved by the action of dilute hydrochloric acid on 25 grams of zinc? Zn = 65. [C. 08].

7. What weight of sulphuric acid and zinc would theoretically be required for the reduction of 10 grams of copper oxide? [A. 98].

For solution of problems see typical examples, Chap. XII.

CHAPTER XVIII.

OXYGEN AND OZONE.

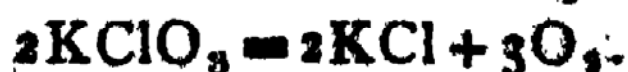
† OXYGEN.

ATOMIC WEIGHT 16. DENSITY 16. MOLECULAR FORMULA O_2 .

Occurrence.—Oxygen is found most abundantly in nature. In the free state it constitutes about $\frac{1}{5}$ of the volume of the air, and in combination with hydrogen it constitutes $\frac{8}{9}$ of the weight of water. It is also a main ingredient of the earth's solid crust and of animal and vegetable bodies.

Preparation.—Oxygen is prepared by decomposing (1) certain salts rich in oxygen and (2) peroxides: these being heated either alone or sometimes with sulphuric acid. Other sources of the gas are (3) water and (4) atmospheric air.

(1) The *laboratory method* is to heat potassium chlorate (KClO_3). This salt melts at a fairly high temperature, yielding potassium chloride and pure oxygen. A strong flask or retort is required for the reaction, and the heat has to be regulated carefully. The gas is collected over the pneumatic trough.



If potassium chlorate be intimately mixed with one-third

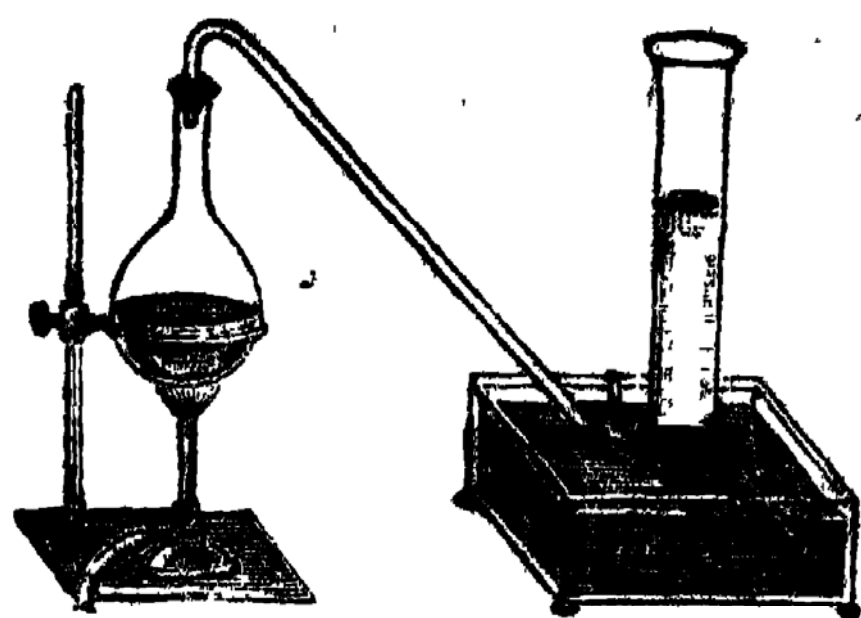


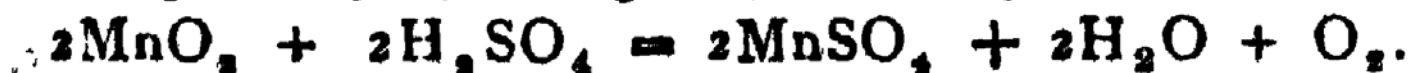
Fig. 26.

of its weight of manganese dioxide (MnO_2), and the mixture is then heated, oxygen is given off readily at a lower temperature. In this case, potassium chlorate alone is decomposed: the manganese dioxide acts as a *catalytic agent* (p. 12).

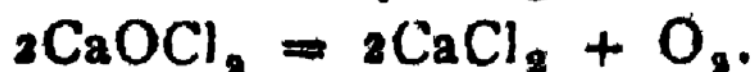
Other salts which when heated singly or with sulphuric acid yield oxygen, are the nitrate (KNO_3), permanganate (KMnO_4), and bichromate of potassium ($\text{K}_2\text{Cr}_2\text{O}_7$).



(2) Manganese dioxide and lead dioxide are examples of peroxides which on similar heating evolve oxygen.



Oxygen from Bleaching-powder.—A ready supply of oxygen is obtained by gently heating a mixture of cobalt oxide and bleaching-powder (CaOCl_2) made into a thin paste with water. The cobalt oxide here acts as a catalytic agent.



(3) Oxygen is obtained from water, either (a) by *electrolysis*, or (b) by decomposing steam by means of chlorine. A mixture of steam and chlorine being passed through a red-hot porcelain tube containing pumice, the chlorine unites with the hydrogen of water and oxygen is set free. $[2\text{Cl}_2 + 2\text{H}_2\text{O}$

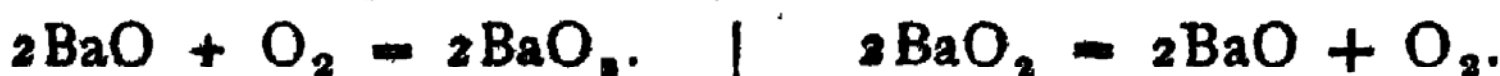
$= 4 \text{ HCl} + \text{O}_2$]. On bubbling the resulting mixture through a solution of caustic soda or potash, hydrochloric acid gas is absorbed and pure oxygen issues out.

(4) Oxygen is removed from air (a) indirectly by Priestley's method or by Brin's process, and (b) directly by fractional distillation of liquid air:—

Priestley's and Lavoisier's Method.—Mercury is heated for some time in the air, and is changed into a red powder (mercuric oxide, HgO). This oxide, when further heated, is decomposed into mercury and oxygen (p. 8):



Brin's Manufacturing Process.—Baryta (barium monoxide, BaO) when heated in the air, forms barium dioxide (BaO_2) which on further heating liberates oxygen:



This method, known as Brin's process, is employed for the *manufacture* of oxygen. Air under pressure is forced over heated baryta; the oxygen of the air combines with baryta, forming BaO_2 , and the unused nitrogen passes off. On removing the pressure, BaO_2 liberates oxygen which is pumped out by means of vacuum pumps, and baryta remains behind. By repeating these operations continuously, a large quantity of oxygen is collected.

Manufacture from Liquid Air.—The recent mechanical process of manufacturing oxygen is to subject liquefied air to fractional distillation: by this means the more volatile nitrogen escapes, leaving behind oxygen which is then compressed into tanks or cylinders.

Properties: Physical.—Oxygen is a colourless, tasteless, and inodorous gas; it is slightly heavier than air. Oxygen is the supporter of respiration; it is essential to the life of animals and of plants. If, however, an animal be kept in pure oxygen, its life-processes will be so energetic that it will rapidly emaciate. The gas is very slightly soluble in water;

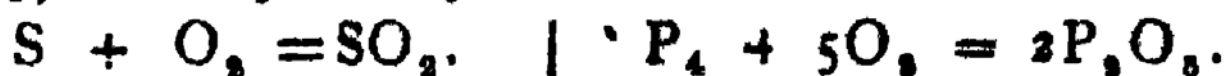
but the little quantity of it absorbed by water makes the breathing of fishes possible.

Chemical.—Oxygen is a very active agent; it combines with almost all elements, forming *oxides*. It is a great supporter of combustion; *all inflammable bodies burn brilliantly in oxygen*. This may be illustrated by the following experiments:

(1) A piece of charcoal, *i. e.* carbon (C), when kindled in a deflagrating spoon and plunged into a bottle of oxygen, burns brilliantly. The gas produced in the bottle by the combustion is carbon dioxide (CO_2), which will turn lime-water milky.



(2) Sulphur and phosphorus, when similarly treated, burn very brightly. Sulphur dioxide (SO_2) and phosphorus pentoxide (P_2O_5) are respectively formed:



SO_2 and P_2O_5 can be dissolved in water, and the solutions will turn blue litmus red, thus proving that they are *acids*.

(3) Sodium and magnesium burn in oxygen, forming the respective oxides:



These oxides are white solids which are soluble in water and turn red litmus blue; they thus form *bases*.

(4) Iron, which does not burn in the air, burns in oxygen.

Thus, when a steel watch-spring is tipped with burning sulphur and then plunged in a stout jar of oxygen, the spring burns with brilliant scintillations and drops of molten iron oxide are thrown off. [$3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$]. The oxide will be found to be insoluble in water, and will have no action on litmus.

NOTE.—As in some of the above experiments acid-forming oxides were formed by the union of the gas with other elements, Lavoisier named the gas 'oxygen,' *i. e.* acid-generator. It must now however be said that the name is a misnomer. See p. 88.

Tests.—A glowing splinter of wood when introduced in oxygen bursts into flame. But as this property is also possessed by nitrous oxide (N_2O), the two gases can be distinguished

thus : oxygen by combining with nitric oxide (NO) produces reddish-brown fumes ; while nitrous oxide does not do so.

Oxides.—Oxides are the compounds of elements with oxygen. They may be roughly divided into four classes :

(1) *Acidic oxides, i. e.* oxides (usually of non-metals) which by union with water form acids ; such are carbon dioxide (CO_2), sulphur dioxide (SO_2), phosphorus pentoxide (P_2O_5), &c.

(2) *Basic oxides, i. e.* oxides (usually of metals) which neutralize acids to form salts and water. Some of these oxides unite with water to form bases. Sodium oxide (Na_2O), calcium oxide (CaO), barium oxide (BaO) are examples.

(3) *Neutral oxides, i. e.* oxides which are neither acidic nor basic. Such are water (H_2O), iron tetroxide (Fe_3O_4), &c.

(4) *Peroxides, i. e.* oxides which contain more oxygen than acidic or basic oxides, and which give off a portion of their oxygen when heated. Barium peroxide (BaO_2), manganese dioxide (MnO_2) are examples. All metallic peroxides when heated with sulphuric acid evolve oxygen (besides producing salts and water) ; while some of them evolve chlorine on heating with hydrochloric acid.

OZONE.

MOLECULAR WEIGHT 48. DENSITY 24. FORMULA O_3 .

Occurrence —Ozone occurs in small quantities in the air, near the sea-side and in open plains. It is formed when an electric machine is at work and during thunderstorms.

Préparation.—(1) Ozone, mixed with nearly 90 per cent. of oxygen, is prepared by the action of silent electric discharge on dry oxygen.

[We take a narrow glass tube, coil round it a piece of platinum wire, and down its inside pass another platinum wire which must come out through the walls of the tube. We then pass a slow current of oxygen into the tube, and connect the two ends of the



Fig. 27.

wires with a powerful electric machine. A mixture of oxygen and ozone comes out from the other end of the tube.

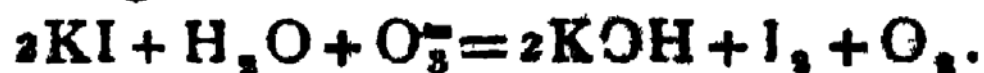
An improved form of the above apparatus, known as *Siemen's ozone tube*, consists of two glass tubes, one inside the other. Here oxygen is ozonized in the annular (ring-like) space between the two tubes].

(2) Ozone is produced, along with oxygen, during the electrolysis of acidulated water.

(3) Ozone is also formed when phosphorus is allowed slowly to oxidize in moist air.

Properties : Physical.—Ozone is a colourless gas having a characteristic fishy smell (whence the name 'ozone' meaning 'smell'). It is slightly soluble in water, but is absorbed by oil of turpentine. It can be condensed to a deep blue liquid which is explosive and at temperatures of 250° to 300°C . it is reconverted into oxygen.

Chemical.—Ozone is called *active oxygen*. It supports combustion, and is a powerful oxidizing and bleaching agent. This is due to the fact that when ozone is decomposed the nascent oxygen acts very energetically. Ozone destroys cork and india-rubber, and bleaches vegetable colours. Metals which are acted upon by oxygen with difficulty, are readily attacked by ozone: thus mercury by contact with ozone is converted into its oxide. Ozone decomposes a solution of potassium iodide, liberating iodine:

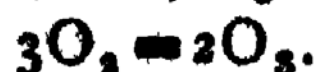


Test—A solution of potassium iodide and starch is turned blue by ozone.

Ozone is an allotrope of Oxygen : Composition of Ozone.—Ozone is an allotropic modification of oxygen: whilst a molecule of oxygen consists of two atoms, a molecule of ozone is composed of three atoms of oxygen. This is evident from the following experimental facts—

(1) *Ozone is converted by heat into ordinary oxygen, and its volume is then increased from two to three.* Hence we have the equation: 2O_3 (4 vols.) $= 3\text{O}_2$ (6 vols.).

(2) *Oxygen, when converted into ozone, contracts to two-thirds its original volume.* [When we ozonise a measured quantity of oxygen a contraction (say of 1 volume) takes place. On absorbing the ozone by turpentine, a further contraction of 2 volumes is observed. Thus the ozone occupied 2 volumes and it was produced from $(2 + 1) = 3$ volumes of oxygen].



(3) *When ozone oxidizes potassium iodide there is no diminution in the volume of the gas.* [This is explained if we represent a molecule of ozone by the formula O_3 . On its decomposition, an atom of oxygen would act on the iodide, and a molecule of oxygen (O_2) would be set free—this oxygen molecule occupying the same volume as the original ozone molecule (Avogadro's Law). For equation see above].

(4) *The density of ozone, as determined from its rate of diffusion, is found to be nearly 24.* Hence its molecular weight must be $24 \times 2 = 48$, i. e. thrice the atomic weight of oxygen. Thus the molecular formula of ozone is O_3 .

University Examination Questions.

I.

1. Describe how you would prepare oxygen in the laboratory and give a careful sketch of the apparatus you would employ. What are the reactions occurring in the preparation of oxygen on the large or manufacturing scale, and what are the conditions under which these reactions are carried out? [C. 1900].

2. How would you show that oxygen can be obtained from lead nitrate? Sketch the apparatus you would use for the experiment. Give equation. [C. 1914].—[See preparation of Nitrogen Peroxide].

3. How much Potassium Chlorate would you take to prepare 5 grammes of oxygen? [C. 92].

4. What are the *oxides*? How would you classify them? Describe the preparation and properties of one member of each class [C. 1912].

Classify the oxides. Give reasons for the scheme you adopt and the characteristic properties of each class. Illustrate your

answer by reference to Al_2O_3 , Cu_2O , Fe_3O_4 , NO , MnO_2 , P_2O_5 , PbO , Pb_3O_4 . [A. 1914].

II.

1. Compare the allotropic forms of oxygen [C. 92, 1900, 1911 ; A. 94, &c.]

2. How is ozone prepared? [C. 92 ; A. 01, 1912]. Describe its properties and show how you can prove its constitution [A. 01, 08, 1912].

3. Oxygen and ozone are said to be allotropic forms of one element. Give reasons for the statement [C. 06 ; A. 1913, 15]. The formula O_3 is assigned to the molecule of ozone. Give experiments showing the facts which justify this formula [C. 07]. How would you prove that *three* volumes of oxygen condense to form *two* volumes of ozone? [A. 07].

CHAPTER XIX.

OXIDES OF HYDROGEN.

WATER (HYDROGEN MONOXIDE).

FORMULA H_2O . MOLECULAR WEIGHT 18. VAPOUR DENSITY 9.

Sources and Varieties of Natural Water.—The sources of water found in nature are (1) rain and snow, (2) springs, (3) rivers, and (4) the sea. The characteristics of these varieties of water are the following—

(1) Rain water.—It is the purest form of natural water. But in its passage through the atmosphere, rain water takes up many impurities, e. g. oxygen, carbon dioxide, traces of ammonia, sulphur dioxide, common salt, particles of soot and organic matter floating in the air.

(2) Spring water.—It is clear and transparent, but contains in solution salts of calcium, magnesium, &c., derived from the soil through which the water percolates and issues out.

(3) River water.—It is generally turbid, owing to its holding insoluble matter in suspension. It also contains dissolved impurities and is often polluted with sewage, refuse, and putrid matter.

(4) Sea water.—It contains in solution the largest amount of solid matter, of which common salt is the chief.

Mineral and Fresh waters.—A water which contains so much dissolved impurities that it has a distinct taste or some medicinal effect, is called a *mineral water*. A water which does not hold such impurities in solution is called *fresh water*. For example, sea water is mineral water, while rain-water is fresh.

Hard and Soft waters.—A soft water is one which gives a lather with very little soap, while a hard water is one which does not give a lather until much soap has been used. The hardness of water is due to its containing calcium and magnesium salts. Rain water is soft, river water is either hard or soft, spring water is generally hard, sea water is always hard.

The behaviour of hard water with soap is explained thus :— Soap is a kind of salt. The calcium or magnesium salt present in hard water acts upon the soap, producing an insoluble compound which is precipitated as a curdy solid. The soap is thus destroyed, and it cannot dissolve in the water and so form a lather until all the calcium or magnesium is precipitated.

Temporary and Permanent Hardness.—The hardness of water may be temporary or permanent, or both at the same time. *Temporary hardness* is that which can be removed by boiling the water, and is due to the presence of *bicarbonate* of calcium or magnesium.

When water containing carbon dioxide flows over carbonate of calcium or magnesium, the soluble bicarbonate is produced and the water becomes temporarily hard. When such water is boiled, the bicarbonate is decomposed; the insoluble carbonate being again formed and thrown down. Thus—



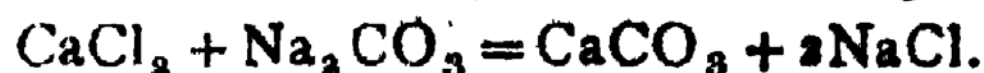
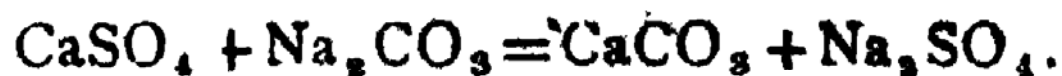
The *fur* or solid crust that accumulates in kettles and boilers is carbonate of calcium or of magnesium, deposited from boiling water, as explained above.

Permanent hardness is that which cannot be got rid of by boiling the water, and is due to the presence of *sulphates* or *chlorides* of calcium and magnesium.

Softening Hard Water.—(1) *Temporary hardness of water can be removed by boiling it or by adding lime to it.* The latter method is known as Clark's process, and consists in adding the required quantity of slaked lime (CaH_2O_2) to a given quantity of the water. By this means all the lime is precipitated as carbonate :



(2) *Permanent hardness of water can be removed by adding to it washing-soda, i.e. sodium carbonate, Na_2CO_3 .* By this means the sulphate or chloride present in the water is decomposed, and carbonate of calcium or magnesium is precipitated :



Water thus softened is suited for washing purposes, but not rendered potable (on account of the presence of the sodium salt).

Purification of Water.—The foreign matter contained in water may be held in suspension as well as in solution. To purify water we have therefore to adopt the following methods :

1. *Filtration.*—Filtration through beds of sand and gravel removes insoluble or suspended impurities.

2. *Distillation,*—this separates all soluble or dissolved impurities. But in order to get rid of volatile impurities, we have also to add a strong solution of potassium permanganate and caustic potash, before distillation. The first and last portions of the distillate are rejected ; the middle portion is pure water. [For form of apparatus see Fig. 12].

Physical Properties of Water.—Pure water is tasteless and inodorous ; it appears colourless in thin layers, but in large masses or thick layers it has a faint greenish-blue colour. Its specific gravity is 1 ; that is to say, water is chosen as the

standard for comparing the weights of equal volumes of solids and liquids. Water is almost incompressible.

Effect of Heat and Cold on Water.—Water is a liquid at ordinary temperatures. It expands when heated, and at 100°C . it boils and is converted into an invisible vapour (which when partly condensed is popularly called *steam*). One volume of water becomes nearly 1600 volumes of vapour at 100°C .

When cooled, water gradually contracts until it reaches the temperature of 4°C . At this temperature water has its maximum density. Cooled below 4°C ., water again expands until it reaches 0°C . when it solidifies into ice. Ice is therefore lighter than liquid water: 10 volumes of water form nearly 11 volumes of ice.

Water (as well as other non-metallic liquids) are very bad conductors of heat. We can heat the upper layers of water contained in a tube without affecting the temperature of the layers at the bottom. Thus water (as well as other liquids) has to be heated from below: the particles at the bottom being heated, expand, rise up, and impart the heat to the next upper particles,—the process going on until the heat is distributed uniformly throughout the whole mass. This process of transmission of heat is called *convection*.

Chemical Properties of Water.—Water is a neutral substance, *i. e.* it is neither an acid nor a base. It exists in large proportions in all vegetable and animal substances. It combines energetically with quicklime, oxide of phosphorus, and sulphuric acid; it also unites loosely with many salts, when it is known as *water of crystallization*. Water does not ordinarily act chemically with metals; but it is decomposed by sodium and potassium, and steam is decomposed by red-hot iron.

Water dissolves the largest number of substances. It is therefore generally found to be mixed up with impurities or foreign substances.

Volumetric Composition of Water.—The composition of water by volume is determined by the following methods :

(1) **Electrolysis.**—See p. 9. This is the *Analytic Method* of proving the composition of water ; the following are the *Methods of Synthesis*.

(2) **Eudiometer Experiments.**—The volumetric composition of water is best studied in experiments made with a eudiometer (*i.e.* an instrument used to study the composition of gaseous bodies by means of an electric spark).

(a) **Cavendish's Method.**—The true composition of water was first demonstrated by Cavendish. The apparatus he used (now

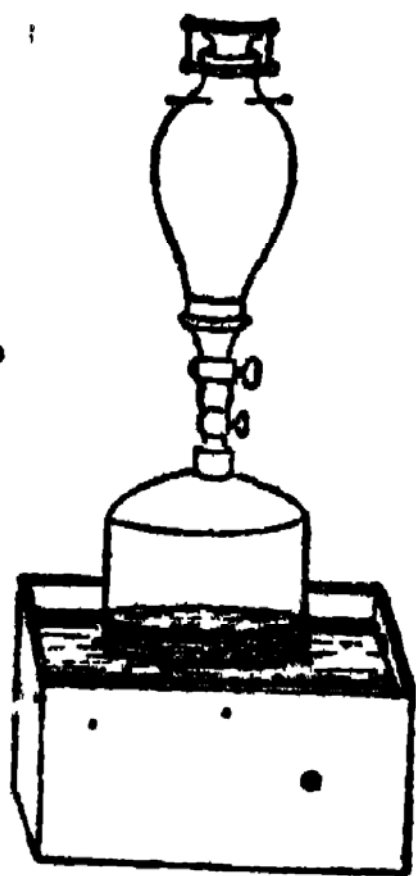


Fig. 28.

known as 'Cavendish eudiometer') consists of a pear-shaped bottle or globe, provided with two platinum wires fused through its top and with a stopcock at its bottom. The eudiometer is first exhausted of air and then screwed on to a gas cylinder standing over mercury and containing a mixture of 2 volumes of hydrogen and 1 volume of oxygen. On opening the stopcocks the mixed gases enter the eudiometer. If now the taps are closed and an electric spark passed through the wires, the

mixed gases explode and combine to form water which appears as dew on the inner sides of the eudiometer. The vessel is now practically vacuum (neglecting the thin film of dew contained in it) and may be again filled with the mixed gases which may be exploded. By repeating the experiment several times, an appreciable quantity of pure water will be produced in the eudiometer.

(b) **Hofmann's Method.**—By this method we can ascertain the volumetric composition of water in the form of *steam*. We take a U-shaped eudiometer, *i.e.* a U-tube having one limb

open and having two platinum wires fused through the closed limb which is graduated. The closed limb is first filled with dry mercury and then a mixture of two volumes of hydrogen and one volume of oxygen is introduced in it. The closed limb is also surrounded by a wider tube through which passes the vapour of boiling amyl alcohol (which boils at 132°C). [By this means the mixed gases in the closed limb are constantly kept at a temperature above 100°C .]

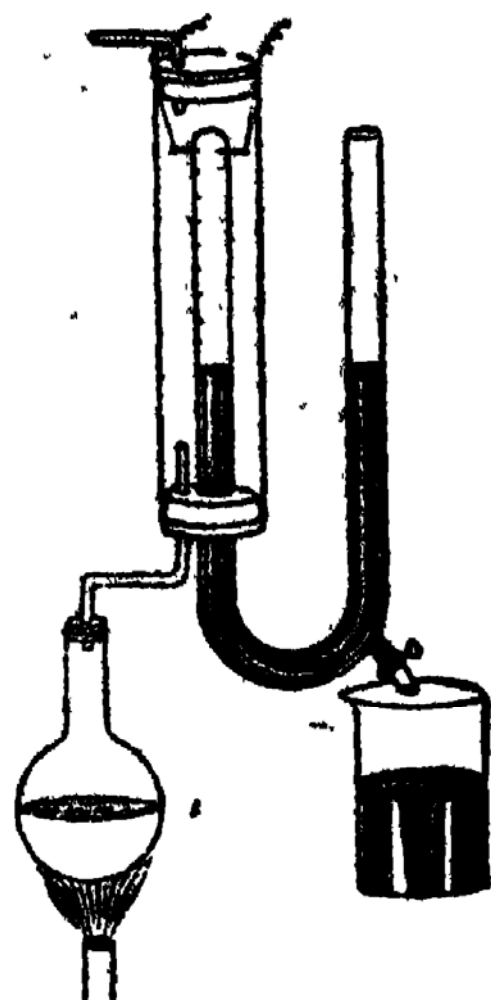


Fig. 29.

When the amyl vapour has passed for some time, the mercury is brought to the same level in the two limbs of the tube (so that the mixed gases might be under the ordinary atmospheric pressure), and the volume of the mixed gases carefully noted. [Some more mercury is withdrawn at this stage, so that the gases being under decreased pressure the apparatus would not be shattered by the explosion]. The open end is then firmly closed and an electric spark passed through the wires. The resulting gas will contract in volume. Mercury is then added to bring it to the same level in the two limbs, and the gaseous volume again measured. The volume will be found to be only two-thirds of the original volume. Hence, 2 volumes of hydrogen by uniting with 1 volume of oxygen produce 2 volumes of steam.

Gravimetric Composition of Water.—The composition of water by weight has been carefully determined by Dumas and others. The following is a rough outline of the method adopted :

Pure dry hydrogen is passed over a known quantity of heated copper oxide contained in a bulb. The hydrogen reduces the oxide to metallic copper and unites with oxygen to form water which is absorbed



Fig. 30.

by a known weight of calcium chloride contained in a U-tube.



The gain in weight of the calcium chloride indicates the quantity of water formed; and the loss in weight of the copper oxide gives the weight of oxygen that has combined to form the water. The difference of these two weights represents the weight of hydrogen used. By careful experiments Dumas found that in 100 parts of water there are nearly 88.9 parts of oxygen and 11.1 parts of hydrogen. In other words, oxygen and hydrogen unite nearly in the proportion of 8 : 1 by weight.

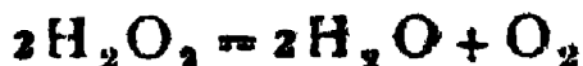
• HYDROGEN DIOXIDE OR PEROXIDE.

FORMULA H_2O_2 . MOLECULAR WEIGHT 34.

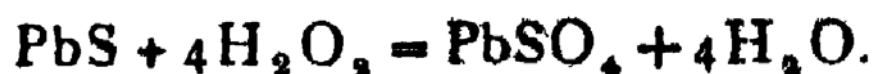
Preparation.—It is prepared by the action of dilute sulphuric acid (or any other suitable acid) on barium dioxide :



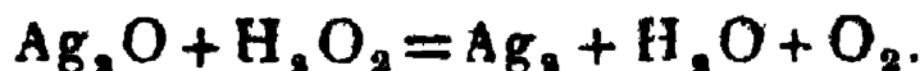
Properties.—Hydrogen dioxide is known in aqueous solution only. In a concentrated form it is a colourless, inodorous, syrupy liquid, with an astringent taste. It is an unstable compound, readily decomposing by heat into water and oxygen :



It is a powerful oxidizing agent having bleaching properties. Lead sulphide is oxidized by it into lead sulphate :



Hydrogen dioxide sometimes appears to act also as a reducing agent. This is due to its loose oxygen atom readily uniting with another feebly combined oxygen atom of some other compound. Thus when it acts on silver oxide, oxygen is evolved and the oxide is reduced to metallic silver.



Test.—Hydrogen peroxide liberates iodine from potassium iodide in presence of ferrous sulphate. [Compare tests for ozone, chlorine, and nitrogen trioxide or the nitrites]

Uses.—Besides its use in medicine, hydrogen peroxide is used in restoring the colour of old oil-paintings and in bleach-

ing feather, hair, ivory, silk, sponge, &c. It is also valuable in Quantitative Analysis.

University Examination Questions.

1. What impurities are commonly present in ordinary water? Describe the experiments by which you have become aware of their presence, mentioning the source from which you derived the samples with which you made your experiments [C. 09].

2. Explain the terms temporary and permanent hardness of water [C. 99 ; A. 15]. Distinguish between temporary and permanent hardness of water and state their causes [C. 06].

What is the chemical nature of the sediment formed in kettles in which hard water has been boiled, and why is it formed? If you treat the sediment with hydrochloric acid, what reaction takes place? [A. 05].

What causes hardness, and how is it removed in practice? [C. 1916 ; A. 1915].

What is Clark's process of softening water? [C. 06] How can permanently hard water be softened? [C. 99].

3. What *impurities* would you expect to find in a specimen of *river water*, and how would you proceed to prepare a specimen of pure water from it? Give a sketch of the apparatus you would employ [C. 1912]. Some muddy river water is given to you: describe the method you would employ to get rid of—(a) the suspended, and (b) the dissolved impurities. Make a sketch of the apparatus you would employ in the second case [A. 02]. How could you obtain pure water from ordinary water. Sketch and explain the apparatus you have used for that purpose. Can you remove all the impurities by this means? If not, why not? [C. 09].

4. How can you show that water consists of the elements hydrogen and oxygen? [C. 98, 1910].

5. Describe how you would demonstrate the composition of water by volume and by weight [C. 94].

State clearly what you understand by the formula H_2O . Describe without going into minute detail, how it has been proved that this formula correctly represents the composition of water [C. 97].

How could you show the composition of water (1) analytically, (2) synthetically? [A. 04]. By what experiment can the composi-

tion of steam by volume be proved synthetically? Describe the experiment in detail, and make a sketch of the apparatus required [C. 1900, 15]. Describe experiments showing that when two volumes of hydrogen combine with one volume of oxygen, the resultant compound occupies two volumes in the gaseous condition [C. 09].

How can the composition of water be determined gravimetrically? [A. 99]

CHAPTER XX.

NITROGEN AND THE ATMOSPHERE.

NITROGEN.

ATOMIC WEIGHT 14. DENSITY 14. MOLECULAR FORMULA N_2 .

Occurrence.—Nitrogen occurs in the free state in the air, forming nearly $\frac{4}{5}$ of its bulk, the remaining $\frac{1}{5}$ being oxygen. In combination with other elements it is found in animals and plants, and in potassium nitrate (KNO_3), commonly known as saltpetre or *nitre*,—whence the name 'nitrogen' is derived.

Preparation.—1. Nitrogen (mixed with 1 per cent. of argon) is prepared *from the air by removing oxygen from it*, by the following two processes:

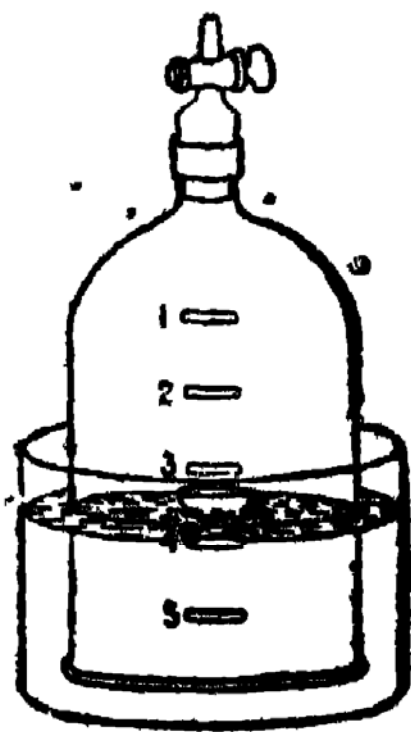


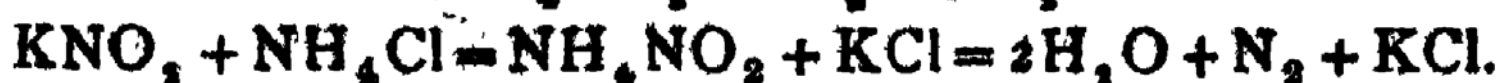
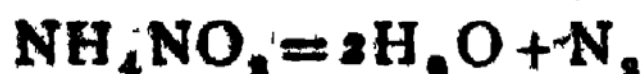
Fig. 31.

(1) By igniting a piece of phosphorus in a porcelain crucible floating on water, and then quickly covering it with a bell jar, the phosphorus unites with the oxygen of the air in the bell jar, forming dense white fumes of phosphorus pentoxide (P_2O_5) which are speedily dissolved by water so that only nitrogen is left in the bell jar.



(2) By passing pure air over red-hot copper contained in a hard-glass or iron tube, the oxygen of the air unites with copper forming cupric oxide, and only nitrogen passes over and may be collected over the pneumatic trough. [See below, Dumas's method of determining the Composition of Air].

II. Pure nitrogen is prepared by heating ammonium nitrite (NH_4NO_2), or instead of it, by boiling a solution of potassium nitrite (KNO_2) and ammonium chloride (NH_4Cl):



III. It is also obtained by passing chlorine over an excess of ammonia. On passing chlorine gas through a strong solution of ammonia, nitrogen is evolved: hydrochloric acid which is also produced unites with the excess of ammonia to form ammonium chloride. [In this experiment the ammonia must be in excess; otherwise the violently explosive chloride of nitrogen will be formed].



Properties: Physical.—Nitrogen is a colourless, tasteless, and inodorous gas. It is slightly lighter than air, and is very slightly soluble in water. It is not poisonous; but it does not support respiration: hence its old name *azote*. It serves the useful purpose of diluting the oxygen of the air.

Chemical.—Nitrogen is inert or inactive, *i.e.*, it does not readily combine with any other element. It is neither inflammable, nor a supporter of combustion.

Under the influence of sparks from an induction coil, nitrogen combines with oxygen and with hydrogen, producing small amounts of nitrogen tetroxide (NO_2) and ammonia (NH_3) respectively. Boron, silicon, lithium, calcium, magnesium and some other elements also unite with nitrogen at red-heat, forming *nitrides*.

By the action of a powerful electric discharge nitrogen is said to undergo partly an allotropic modification. This allotropic nitrogen glows spontaneously, combines with ordinary phosphorus, and exhibits other active properties.

THE ATMOSPHERE.

Constituents of the Air.—The atmosphere or air we live in is principally a mixture of the two gases oxygen and

nitrogen approximately in the proportion of one to four :
21 per cent. oxygen and 79 per cent. nitrogen by volume.

23 " " " " 77 " " " " weight.

But besides these two gases, there are other substances present in the air in small but variable quantities. The average proportions of all the constituents in 100 volumes of pure air are the following :

Oxygen	20.65 volumes
Nitrogen	77.11 "
Argon (and neon, krypton, xenon)			0.8 "
Water-vapour	1.4 "
Carbon dioxide	0.03 "
Ozone	}	...	traces.
Ammonia			
Nitric acid			

The air in large towns and badly ventilated rooms contains many impurities, such as sulphuretted hydrogen, sulphur dioxide, particles of soot, bacteria, &c.

Of the several essential constituents of the air, oxygen is the supporter of respiration, nitrogen acts as a diluent thereto, water-vapour appears by condensation as rain and snow, and carbon dioxide (as well as nitrogen) supplies the food to the vegetable kingdom.

Methods of determining the Composition of Air.—That air consists principally of nitrogen and oxygen in the proportion of 4 to 1 nearly, can be experimentally determined by the following methods. The first is the method of determining the proportionate *volumes*, and the second the proportionate *weights* of the constituents.

Eudiometric Method of Cavendish.—A measured volume of pure dry air and half as much hydrogen are introduced into a eudiometer, and exploded with an electric spark. All the oxygen contained in the air combines with hydrogen to form water (which is deposited on the sides of the vessel) and there occurs a contraction of volume of the gas (mainly

nitrogen) left in the tube. Now, as oxygen unites with hydrogen in the proportion of 1 volume to 2 volumes, one-third of the volume that disappeared must have been oxygen, and this volume is found to be nearly one-fifth of the volume of air taken.

Copper Method of Dumas.—A tube (C) is filled with copper turnings, exhausted of air and weighed. It is then connected with a flask (F) which has also been exhausted and weighed. To the other end of the tube are attached U-tubes (P) containing pumice-stone soaked in sulphuric acid, and U-tubes (H) containing caustic potash. The tube (C) is heated to redness, and the stopcocks (*t*) are opened to allow a slow current of air.

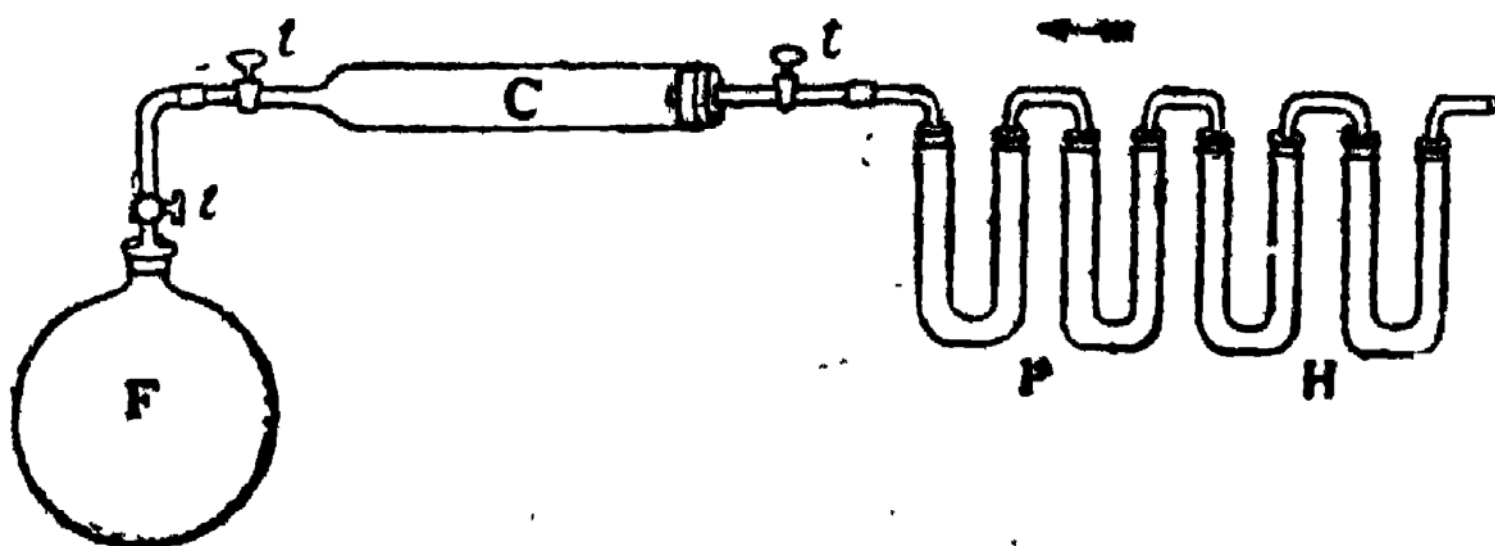


Fig. 32.

As the air passes through the U-tubes, it is freed from carbon dioxide by the caustic potash, and from water-vapour (and traces of ammonia) by the sulphuric acid;* the air is also deprived of its oxygen by the copper, so that only nitrogen passes into the flask. When air has ceased to enter, the stopcocks are closed and the tube C is allowed to cool. The increase in weight of the tube C (now containing copper

* The amount of carbon dioxide and of aqueous vapour present in the air can be determined in this way. When a known volume of air is passed through weighed U-tubes containing H_2SO_4 and KOH, the gain in weight of the H_2SO_4 tubes gives the weight of water absorbed and that of the KOH tubes indicates the amount of carbon dioxide present in the given volume of air.

oxide) gives the weight of oxygen withdrawn from the air, and the increase in weight of the flask gives the weight of the residual nitrogen. The ratio between these two weights is found to be 23 : 77 nearly.

Air is a Mixture, not a Compound.—That air is a mechanical mixture of oxygen, nitrogen, &c., and not a chemical compound of these substances, is evident from the following considerations :

(1) *Synthesis*.—When oxygen and nitrogen are mixed together in the proportion in which they are ordinarily present in the atmosphere, the resulting mixture possesses all the properties of atmospheric air ; and when the gases mix together, there is no change of temperature or volume, as is found in the case of chemical combinations.

(2) *Anomalous composition*.—The composition of air is not always strictly constant ; and the relative weights of oxygen and nitrogen present in air are not simple multiples of their atomic weights (16 and 14).

(3) *Diffusion*.—When air is passed through a porous tube, nitrogen (which is lighter than oxygen) diffuses more readily than oxygen. Had air been a chemical compound its constituents would not have separated in this way.

(4) *Evaporation*.—Nitrogen evaporates from *liquid air* more rapidly than oxygen does. If it were a chemical compound, liquid air would have evaporated as a whole.

(5) *Solubility*.—Oxygen is more soluble in water than nitrogen. Hence, dissolved air which is expelled from water by boiling is found to be richer in oxygen than ordinary air. If air were a chemical compound, solution in water would not alter its composition.

Relation between Animals and Plants.—The animal and the vegetable kingdoms play opposite functions in nature ; but the existence of one is necessary for the existence of the other. Animals live upon plants or vegetable products, which consist chiefly of carbon, hydrogen, and oxygen. The food

of animals partly goes to build up their structure, and partly undergoes a process of combustion (*i. e.* union with the oxygen of the inhaled air), whereby the heat of animal body is maintained and carbon dioxide is given out from the lungs.* [Other sources of the supply of carbon dioxide to the air are the combustion of vegetable matter, and the exhalations from the depths of the earth.].

Plants, on the other hand, have largely to depend on the carbon dioxide of the air. The green parts of plants, with the aid of the sun's rays, decompose the carbon dioxide into carbon and oxygen.† The carbon is used up by the plants in the formation of their tissues, and the oxygen is set free. Plants therefore supply the oxygen which is lost by the air in the respiration of animals and in the processes of combustion, decay, &c. *This interchange of oxygen and carbon dioxide between plants and animals maintains the average constancy in the composition of atmospheric air.*

University Examination Questions.

1.

1. Describe the preparation and chemical properties of nitrogen [C. 95].

2. How may Nitrogen be obtained from (*a*) air ; (*b*) ammonia ; and (*c*) nitric acid ? How would you proceed if you were to prepare a sample of *pure* nitrogen, and why ? [C. 1913].

3. How can Nitrogen be prepared from ammonia, or an ammonium salt ? Calculate the volume of Nitrogen measured at 15°C and 768 mm. obtained from 10.7 grams of ammonium chloride [A. 1910].

* This is proved when we breathe into lime-water : the carbon dioxide in the breath, by union with lime, forms chalk ; and so the water becomes milky. Similarly, moisture is at once deposited on a cold surface against which we may breathe.

† This is demonstrated if we place a fresh water-plant in a bottle of water, and expose the bottle to sunlight : bubbles of oxygen will soon form on the under-surfaces of the leaves of the plant.

II.

1. What is the composition of the Atmospheric Air? State whether it is a true chemical compound or a mere mechanical mixture, giving your reasons for the same; and describe some of the useful purposes served by the different constituents of the Atmospheric Air [C. 92].

2. Mention facts which justify the belief that air is a mixture and not a chemical compound. [C. 96 : A. 14]. What is the relation of air to vegetable life? [C. 96].

3. Give one or more proofs that the atmosphere is not a chemical compound of Nitrogen and Oxygen. What other substances are generally present in air? How could you demonstrate their presence? [A. 99].

4. Describe experiments you would perform to prove the presence of the four important constituents of atmospheric air. What important function has each of these in the economy of Nature? [C. 1913].

How would you prove that the air contains carbon dioxide, and how would you determine the amount? [C. 99, 04 ; A. 03, 14]. Of what use is the carbon dioxide and the nitrogen in the atmosphere? [A. 03].

5. State the composition of air by volume and by weight. [C. 1900].

6. Mention the constituents of atmospheric air, and state the proportions in which the most important of these occur. Describe Dumas' method of determining the composition of air by weight, making a careful drawing of the apparatus used for the purpose [C 09 ; A. 14].

Name the constituents of the atmospheric air, and state how its composition is affected by animal and plant life. Describe simple experiments for determining the quantity by weight of any two constituents of air [C. 1915].

7. How much phosphorus should be burnt to remove the oxygen from 500 grams of air? What will be the weight of the residual gas? How would you ascertain that the gas left after the combustion contains no free oxygen? (The atomic weight of phosphorus is 31). [C. 1900].

8. Find the volume of air, measured at 20°C. and 780 m.m., that would be required for the complete combustion of .5 gram of sulphur. (S = 32, 1 litre of hydrogen at N. T. P. weighs .09 gram). [C. 09].

What volume of atmospheric air measured at 30°C. and 750 m.m. will be required for the complete combustion of one gram of sulphur? (O=16, S=32. Air contains 20·8 per cent. of oxygen by volume, 1 litre of hydrogen at 0°C. and 760 m.m. weighs 0·09 gram). [C. 1911].

9. Air contains 23 per cent. of its weight of oxygen. How many grams of sulphur would be required to burn out the oxygen in 100 litres of air at 30°C. and 755 mm. pressure [C. 1914].

10. 10 cubic centimetres of a mixture of nitrogen and oxygen were mixed with 20 c.c. of hydrogen, and the mixture then exploded. The volume after explosion was found to be 21 c.c. (measured at the original temperature and pressure). Calculate the volumetric percentage composition of the mixture. [A. 1912].

CHAPTER XXI.

COMPOUNDS OF NITROGEN.

SECTION I.

AMMONIA.

FORMULA NH_3 . MOLECULAR WEIGHT 17. DENSITY 8·5.

Occurrence.—Traces of ammonia are found in the air. It is produced in the slow natural decomposition of animal and vegetable bodies, as well as by heating them. The old name for an aqueous solution of the gas is *spirit of hartshorn*, because it was originally prepared by heating the horn, hoof, dung, &c. of harts and other animals.

Preparation.—(1) Ammonia may be obtained by heating any ammonium salt with an alkali. In the laboratory it is usually prepared by heating in a flask a mixture of dry ammonium chloride (NH_4Cl) and quicklime (CaO) or slaked lime (CaH_2O_2): when calcium chloride, water, and ammonia are produced—

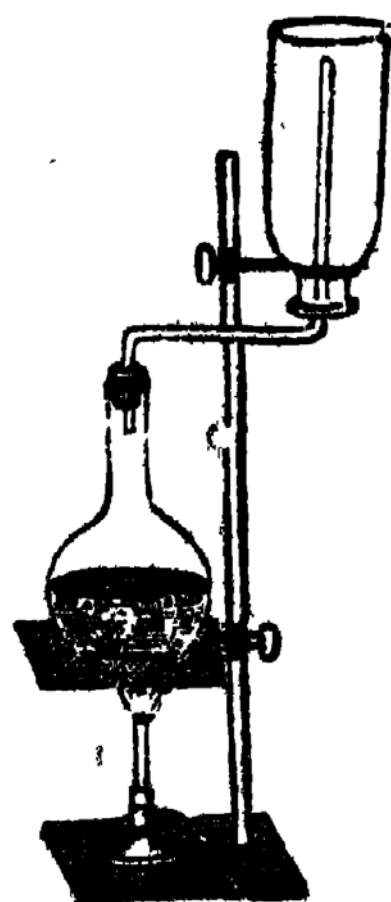
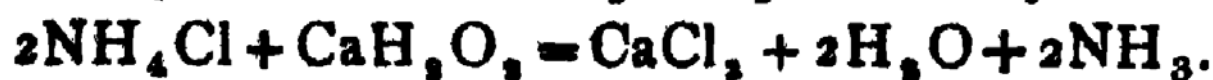
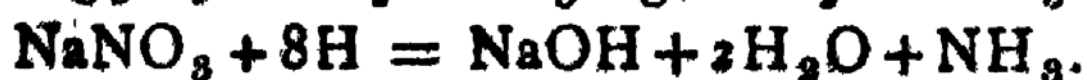
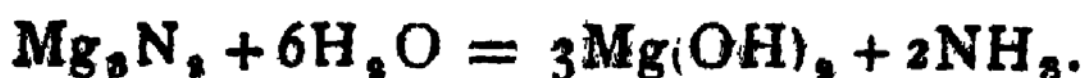


Fig. 33.

As ammonia is lighter than air and soluble in water, it is collected by upward displacement of air (or by displacement of mercury). The gas may be dried by being passed through lumps of quicklime.

Ammonia is also produced (2) by the action of water on magnesium or calcium nitride, and (3) by the action of nascent hydrogen on nitrates or nitrites.



Manufacture.—Ammonia is obtained as a bye-product in the manufacture of coke and coal-gas. Coal contains 2 p. c. of nitrogen, and when it is subjected to destructive distillation one of the gaseous products is ammonia. The resulting mixture of gases being passed through water, all the ammonia is dissolved. This *ammoniacal liquor* is boiled with slaked lime, and the expelled ammonia gas is led into hydrochloric or sulphuric acid. The ammonium chloride or sulphate thus obtained is purified by recrystallization and becomes a ready source of ammonia.

Properties: Physical.—Ammonia is a colourless gas

having a peculiar pungent odour. It is poisonous when inhaled in the concentrated form. It is lighter than air, and is *extremely soluble in water*, one volume of water dissolving at 0°C. nearly 1150 volumes of ammonia.

[The great solubility of ammonia is illustrated by what is known as the *Fountain Experiment*. A round bottomed flask is filled with ammonia and closed with a rubber cork through which passes a long tube furnished with a stopcock.

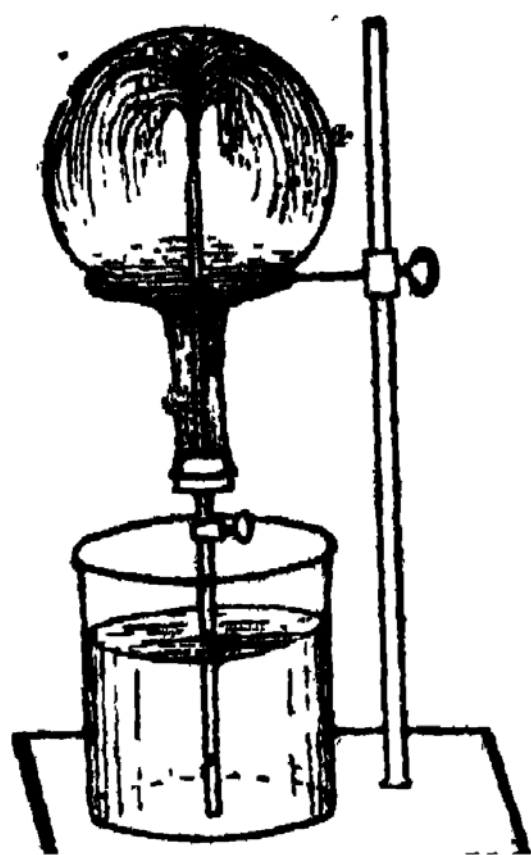


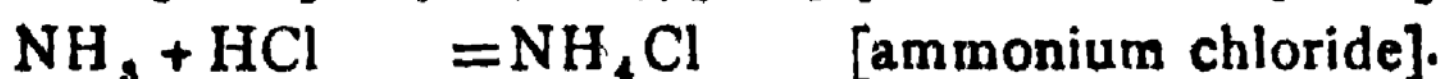
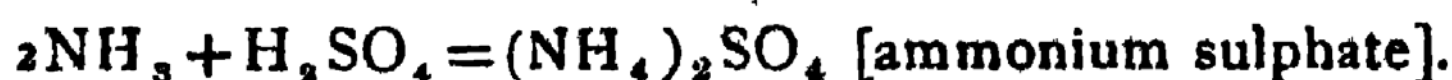
Fig. 34.

The tube is dipped into water which is coloured with red litmus. On cooling the flask with some ether and opening the stopcock,

water rises through the tube and absorbs *all* the ammonia. A vacuum is thus produced within the flask, and so water rushes up into it in the form of a fountain. The water is also turned blue, thus showing that ammonia acts like a base.]

Ammonia is easily liquefied by cold and pressure. Liquid ammonia is extremely volatile, and in its evaporation great cold is produced. Hence the use of ammonia in the preparation of ice by Carre's ice-machine.

Chemical.—(1) *Ammonia behaves like a base.* It turns red litmus blue, and neutralizes strong acids forming salts :

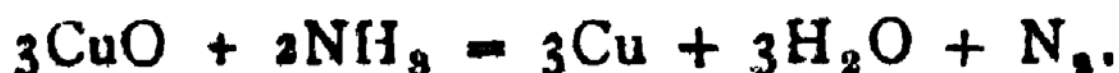


Hence, an aqueous solution of ammonia (NH_4OH) is called 'ammonium hydroxide.' The solution gives off ammonia when heated.

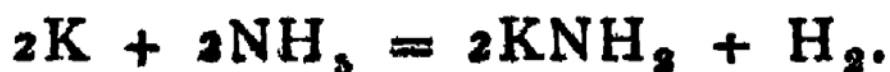
(2) Ammonia does not support combustion, nor does it burn in air ; but it burns in oxygen with a greenish flame.



Ammonia *reduces* cupric oxide and silver oxide when they are heated in it.



(3) When ammonia is passed over heated potassium or sodium, *amide* of the metal is formed.



(4) Ammonia is dissociated into its elements by strong heat or by the passage of electric sparks. It is also decomposed by chlorine and bromine. [See below].

Composition.—The composition of ammonia is shown by the following experiments :

(1) If we pass a series of electric sparks through a known volume of pure dry ammonia contained in a eudiometer standing over mercury, the gas is decomposed (into nitrogen and

hydrogen) and its volume doubled. If we now add sufficient oxygen and pass an electric spark through the mixture, hydrogen and oxygen will unite to form liquid water. On absorbing the excess of oxygen by means of caustic potash and pyrogallic acid, the volume of the residual nitrogen will be seen to be $\frac{1}{4}$ of the volume of the mixture (of nitrogen and hydrogen) obtained after decomposing the ammonia. The

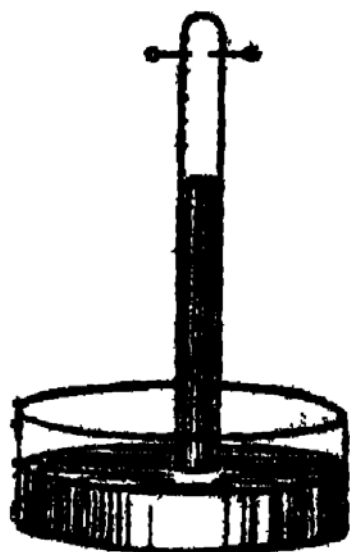


Fig. 35.

diminution of $\frac{3}{4}$ volume must therefore be due to the disappearance of hydrogen that was contained in the mixture.

Hence, by decomposing 1 volume of ammonia we obtain $(2 \times \frac{1}{4})$ volume of nitrogen and $(2 \times \frac{3}{4})$ volumes of hydrogen. That is, 4 volumes of ammonia yield 2 volumes of nitrogen and 6 volumes of hydrogen:



(2) A long tube furnished with a stopcock is completely filled with chlorine, and a strong aqueous solution of ammonia is allowed to fall by drops into the tube through the stopcock. The chlorine combines with the hydrogen of the ammonia (forming HCl) and nitrogen is liberated. On now inverting the tube over water and opening the stopcock, hydrochloric acid gas is absorbed by water which rushes up the tube, and the volume of the residual nitrogen is found to be $\frac{1}{3}$ of the volume of chlorine taken.

But as chlorine combines with an equal volume of hydrogen (to form hydrochloric acid), the volume of the nitrogen must also be $\frac{1}{3}$ of the volume of the hydrogen present in ammonia.

The formula NH_3 .—The densities of ammonia, nitrogen, and hydrogen are 8.5, 14, and 1 respectively. As 4 volumes of

ammonia yield 2 volumes of nitrogen and 6 volumes of hydrogen, the proportions of weights of these volumes are—

Ammonia	...	$4 \times 8.5 = 34$	parts
Nitrogen	...	$2 \times 14 = 28$	„
Hydrogen	...	$6 \times 1 = 6$	„

These numbers are in the ratio of 17 : 14 : 3. Hence, the formula of ammonia is NH_3 . [See pp. 70, 71].

Tests.—(1) Ammonia has its peculiar pungent odour.

(2) It turns red litmus blue.

(3) When a rod dipped in hydrochloric acid is brought in contact with ammonia, dense white fumes (of NH_4Cl) are produced.

(4) When Nessler solution is added to an aqueous solution of ammonia a yellowish or reddish brown tint or precipitate is at once produced. *This is the most delicate test for ammonia and its salts.* [Nessler solution is a solution of the double iodide of mercury and potassium (HgI_2 , 2KI) mixed with caustic potash].

Uses.—(1) In the laboratory, ammonia is valued as a reagent ;

(2) Liquid ammonia is largely used in manufacturing ice ;

(3) Ammonia produces a series of salts (called Ammonium Salts) which are in extensive use for cleansing, dyeing, manuring and other purposes.

Ammonium Salts.—Ammonia (or its aqueous solution, NH_4OH) forms with acids a series of salts which closely resemble the salts of potassium and sodium. Ammonia is therefore called the *volatile alkali*. It is supposed that in these salts the group NH_4 plays the part of a metal : NH_4 is therefore named *Ammonium* and is represented by the symbol Am. Ammonium has not been obtained in the free state, but instead of it we always get ammonia and free hydrogen.

Ammonium salts are mostly prepared from the ammoniacal liquor of gas-works (See above). The chief salts are these :

AMMONIUM CHLORIDE, or *Sal-ammoniac*, NH_4Cl .

AMMONIUM NITRATE, NH_4NO_3 .

AMMONIUM SULPHATE, $(\text{NH}_4)_2\text{SO}_4$.

AMMONIUM SULPHIDE, $(\text{NH}_4)_2\text{S}$.—This salt is prepared by treating ammonia with sulphuretted hydrogen.

AMMONIUM CARBONATES: normal carbonate, $(\text{NH}_4)_2\text{CO}_3$; bicarbonate, NH_4HCO_3 ; carbamate, $\text{NH}_4\text{NH}_2\text{CO}_2$.

Commercial ammonium carbonate (*Sal-volatile*) is a mixture of the latter two compounds, and is prepared by heating together sal-ammoniac and chalk.

Many ammonium salts *dissociate* when heated, and reunite (by sublimation) when cooled. The dissociation of ammonium salts is best illustrated with ammonium chloride. A porous clay pipe is surrounded by a glass tube containing some ammonium chloride. On heating the chloride and passing a current of air through the pipe a mixture of ammonia and air escapes from the pipe and free hydrochloric acid remains within the tube. This shews that ammonium chloride dissociates into its components, NH_3 and HCl , which separate by diffusion.

University Examination Questions.

1. What is the formula for ammonia, its molecular weight and density? [C. 99].

2. Describe the preparation and properties of ammonia [C. 99, 99, &c.; A. 94, 96, 94, &c.]

3. How is ammonia prepared? Give equations [C. 94; A. 99]. Describe, with all experimental details, a method for preparing and collecting a pure dry sample of ammonia gas [A. 1912].

How much ammonia gas would you get from one gram of ammonium chloride at 15°C . and 740 mm.? [C. 1916].

How many grams of ammonium chloride would be required to prepare a cubic metre of ammonia at 15°C . and under 750 mm. pressure? [A. 96].

What weight of ammonium chloride would be required for the preparation of 10 litres of gaseous ammonia at N. T. P.? [C. 92].

What is the ammoniacal liquor of the gas works? [A. 94].

4. If supplied with a number of cylinders of ammonia gas

what experiments would you make in order to illustrate the more important chemical and physical properties of the gas? [C. 1910].

Describe the tests of the gas [C. 09].

5. How would you determine the composition of ammonia? C. 09, 11, 16; A. 99, 04, 06, 09, 11, 15].

Why is ammonia given the formula NH_3 and not N_2H_6 ? [A. 06]. By what experiments would you demonstrate that the formula of the gas is NH_3 ? [A. 1912].

15 c.c. of ammonia gas are completely decomposed by electric sparks in a eudiometer and then 40 c.c. of oxygen gas are introduced and the mixed gases exploded. State the gases present and the volume of each (a) just *before* exploding, and (b) *after* exploding [C. 1913].

SECTION II.

NITRIC ACID.

FORMULA HNO_3 . MOLECULAR WEIGHT 63.

Occurrence.—Nitric acid does not occur in the free state in nature, except in traces in the air. The chief sources of the acid are (1) potassium nitrate (KNO_3 , generally called nitre or saltpetre) which is found as an efflorescence on the soil in India and other hot countries, and (2) sodium nitrate (NaNO_3 , also known as Chili saltpetre or cubic nitre) found in plenty in Chili.

Preparation.—Nitric acid is prepared by the action of strong sulphuric acid on either potassium nitrate or sodium nitrate. In the laboratory, equal parts of nitre and strong sulphuric acid are placed in a stoppered retort, and the mixture is gently heated. Nitric acid distils over and is collected in a receiver kept cool by a stream of water or by being immersed in water.

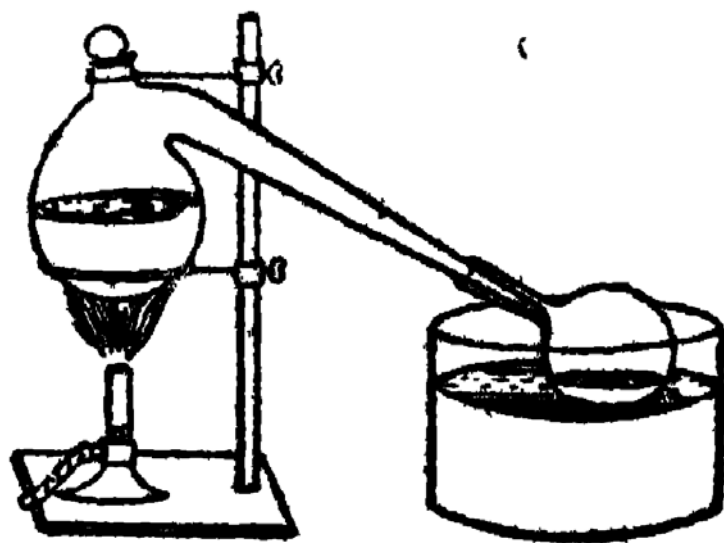
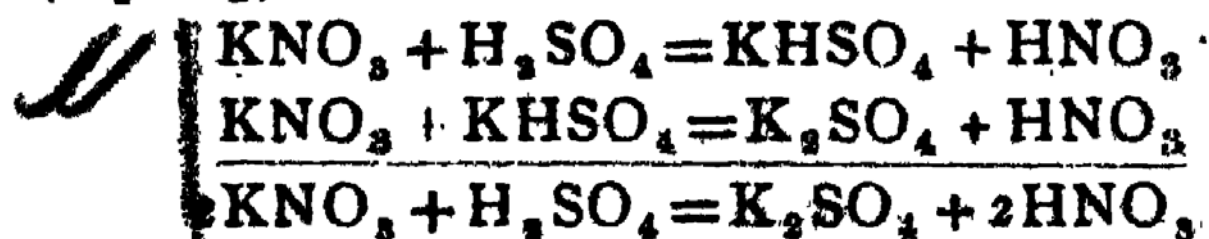


Fig. 36.

The reaction takes place in two stages. At first acid potas-

sium sulphate (KHSO_4) is produced; this reacts, at a higher temperature, upon the nitre and thus normal potassium sulphate (K_2SO_4) is formed.



Manufacture.—Nitric acid is manufactured by heating sodium nitrate and sulphuric acid in large cast-iron retorts lined with fireclay. The acid vapour is carried off through an earthenware pipe into a series of earthenware condensers, and the acid sodium sulphate is run off through an exit pipe. [Usually the reaction is not allowed to go on till the formation of normal sodium sulphate, because the temperature necessary for the purpose decomposes a part of the nitric acid already formed].

Attempts are now being made to manufacture nitric acid by bringing about a direct union of nitrogen and oxygen of the air under the influence of an electric discharge, and then by dissolving the resulting nitrogen peroxide in water.

Pure and Commercial Nitric Acid.—Pure nitric acid is a colourless liquid. But ordinary or commercial nitric acid has a yellowish tinge; it contains about 70 p. c. of the pure acid, the rest being water and oxides of nitrogen. The pure acid is obtained by redistilling commercial nitric acid with sulphuric acid, and then passing a current of dry air through the redistilled acid.

Properties : Physical.—It is a colourless fuming liquid having a peculiar faint choking odour. It is highly hygroscopic. Its specific gravity is nearly 1.5. When heated, nitric acid at first boils at 86° ; but owing to partial decomposition, the acid becomes diluted, and so the boiling-point gradually rises to 120° when the aqueous acid (containing only 68 p. c. of the real acid) distils unchanged. The same aqueous acid is obtained when we distil a diluted acid.

Chemical.—1. *It is easily decomposed by heat*: water, oxygen and nitrogen peroxide (NO_2) being produced.

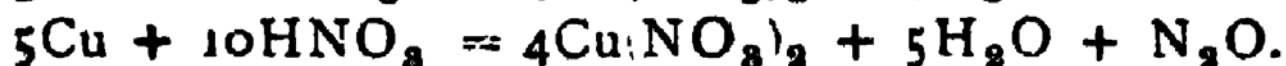
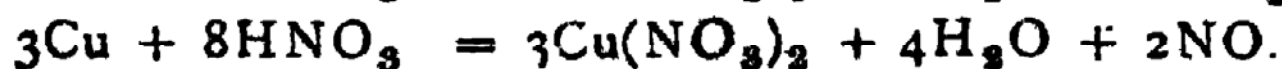
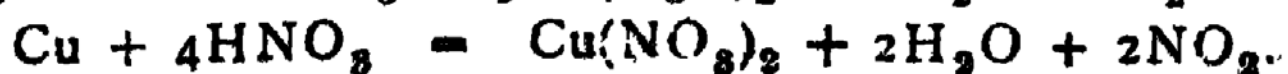
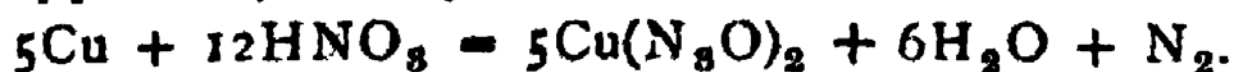


2. *It is a powerful oxidizing agent, and sometimes supports combustion.* Thus, when a stick of glowing charcoal is plunged into the acid, the charcoal bursts into a bright flame. [The charcoal in this case gets oxygen from the liquid acid]. Sulphur and phosphorus when boiled with it are converted into sulphuric and phosphoric acids.

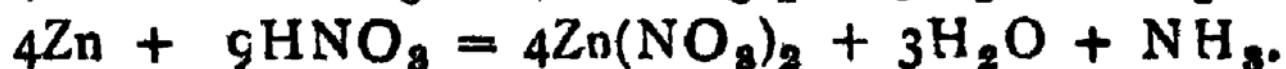
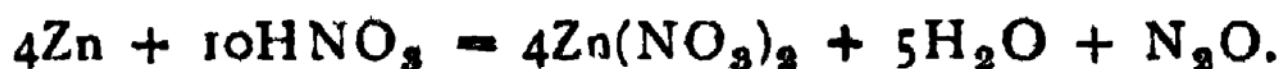
3. *Strong nitric acid violently attacks animal and vegetable bodies.* It corrodes the flesh, and burns wood and clothing. On account of its corrosive and decomposing properties it is called *aqua fortis* (strong water). Dilute nitric acid produces yellow stains on the skin.

4. *Nitric acid dissolves most of the metals.*

Action of Nitric Acid on Metals.—Generally when an acid acts upon a metal, a salt and hydrogen are produced. But when nitric acid acts upon a metal, the liberated (nascent) hydrogen reduces the acid and is converted into water. Hence, *hydrogen is not evolved by the action of nitric acid on a metal.* The result of the action is (1) a nitrate, (2) water, and (3) either nitrogen or generally an oxide of nitrogen. The action depends on the metal, the strength of the acid, and the temperature. For example, the temperature and the degree of concentration of the acid being gradually lowered, its action upon copper may be represented thus—



Similarly, when dilute nitric acid acts upon zinc, nitrous oxide is formed, but when the concentrated acid is used ammonia is the result—

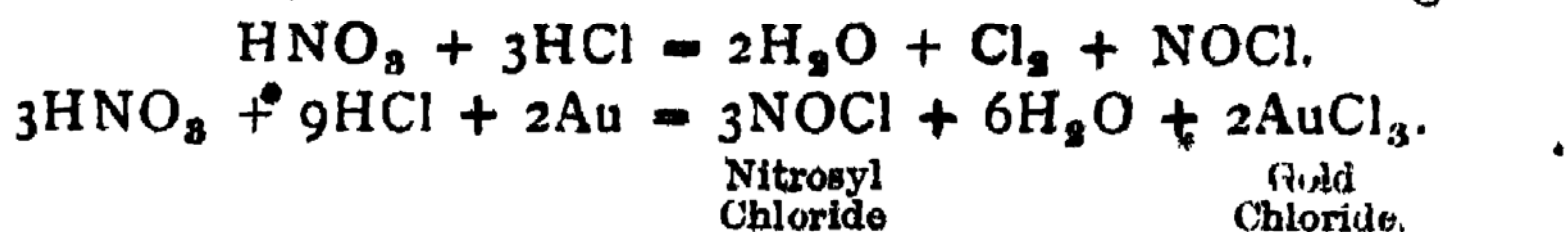


The action of the acid on silver may be represented in one of two ways :



Aqua Regia.—Nitric acid dissolves all the metals, except gold and platinum, upon which the acid has no action. Nor are these two metals affected by hydrochloric or any other single acid. But by mixing together strong nitric acid and hydrochloric acid, a powerful solvent is produced, which dissolves both gold and platinum. This mixture of the two acids is generally called *Aqua regia* (royal water), because it dissolves gold, the 'king of metals.'

The solvent power of *aqua regia* is due to the production of chlorine; and the nascent chlorine combines with gold:



Nitrates.—Nitrates are the salts of nitric acid. They are produced by the replacement of the hydrogen of the acid by a metal or a compound radical, as ammonium (NH_4). Nitre (KNO_3), copper nitrate [$\text{Cu}(\text{NO}_3)_2$], ammonium nitrate (NH_4NO_3) are examples. The characteristics of nitrates are:—

1. *They are soluble in water and form regular crystals.*
2. *They are powerful oxidizing agents:* thus, charcoal burns when it is placed in melted nitre.
3. *They are decomposed by heat, evolving oxygen and nitrogen (or an oxide of nitrogen) and leaving an oxide of the metal behind.* Ammonium nitrate decomposes in an exceptional way, forming nitrous oxide and water.
4. *Their presence is detected by the Ring Test.*

Ring Test.—This is the most delicate test for nitric acid and nitrates. Strong sulphuric acid is added to a solution of a nitrate contained in a test tube, and the mixture is allowed to cool. A solution of ferrous sulphate (FeSO_4) is then carefully poured down the side of the test tube, so that the solution being lighter may rest on the mixture. A deep brown ring will be formed at the point of contact of the two liquids. [Here H_2SO_4 acts upon the nitrate to form HNO_3 ; HNO_3

and FeSO_4 produce nitric oxide which forms the brown compound with FeSO_4].

The uses of nitrates are manifold. They are largely used in medicine, in fire-works, in dyeing, &c. Particularly, nitre is used in manufacturing gun-powder, sodium nitrate as a manure, and silver nitrate in photography.

Tests for Nitric Acid: 1. *Colour Test*.—Nitric acid at once destroys the blue colour of a solution of indigo.

2. *Fume and Colour Test*.—When nitric acid is poured over copper turnings, brown fumes (of nitric oxide) appear, and a blue solution (of copper nitrate) is formed.

3. *Ring Test*.—When ferrous sulphate is gently added to a mixture of nitric acid and sulphuric acid, a brown solution appears in the form of a ring. [See below, Nitric Oxide].

Uses of Nitric Acid.—Nitric acid is employed in dissolving silver and some other metals. It is largely used in the manufacture of sulphuric acid, nitrates, gun-cotton, dyeing colours, &c.

University Examination Questions.

1. Describe the preparation of nitric acid as carried out in the laboratory. [C. 02, 1911]. Sketch the apparatus you have actually used in the preparation of nitric acid. Describe the process of preparation, and mention the principal properties of the compound [C. 1910, 1914 ; A. 1914]. Explain how you would prepare pure nitric acid from ordinary nitric acid. [A. 94]. Describe the properties of nitric acid. State in full the information given by each part and the whole of the chemical equation that represents the mode of its formation [A. 98].

2. Describe what occurs when nitric acid acts upon the following substances, giving equations :—(a) metallic silver, (b) metallic copper, (c) solution of ammonia, (d) charcoal, (e) caustic soda. [C. 94]. What is the action of this acid on silver, copper, and gold ? [C. 02 ; A. 1914]. Describe the effect of strong nitric acid on (a) leather, (b) cotton, (c) a silver coin, (d) gold-leaf, (e) charcoal. [C. 1911].

3. What is *Aqua regia*? [A. 94].
4. Enumerate the chief uses of nitric acid for industrial purposes [C. 1911].

SECTION III.

OXIDES OF NITROGEN.

There are five compounds of nitrogen with oxygen, *viz.*—

N_2O , Nitrogen monoxide, Nitrous oxide or Laughing Gas.

NO , Nitrogen dioxide or Nitric oxide.

N_2O_3 , Nitrogen trioxide or Nitrous anhydride.

N_2O_4 , Nitrogen tetroxide or Nitric peroxide.

N_2O_5 , Nitrogen pentoxide or Nitric anhydride.

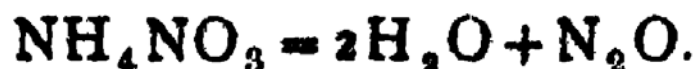
These compounds well illustrate the Law of Multiple Proportions. They are prepared either directly or indirectly from nitric acid, and all of them are decomposed when passed over red-hot copper. The first two oxides are colourless gases, the third is a gas of a brown colour, the fourth condenses to a red liquid, and the fifth is a white crystalline solid. None of the oxides are basic; the last three are acidic.

NITROGEN MONOXIDE OR NITROUS OXIDE.

FORMULA N_2O . MOLECULAR WEIGHT 44. DENSITY 22.

Preparation.—(1) The gas may be obtained by the action of dilute nitric acid on copper or zinc. [See p. 134].

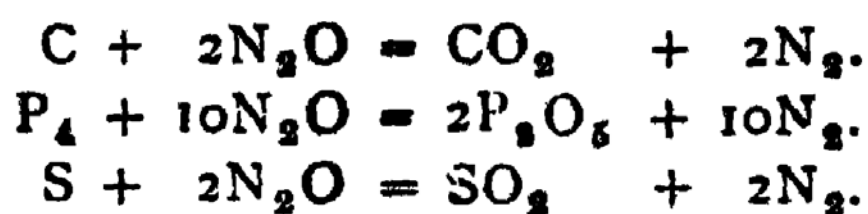
(2) The gas is usually prepared by *gently* heating dry ammonium nitrate (NH_4NO_3) in a flask fitted with a delivery tube⁴ (Fig. 14). It may be purified by passing it through solutions of caustic potash and ferrous sulphate, and is collected over *warm* water or over mercury.



Properties: Physical.—It is a colourless gas having a peculiar sweetish taste and smell. It is $1\frac{1}{2}$ times heavier than air, and is soluble in *cold* water. When inhaled for a short time or in small quantities, nitrous oxide produces a sort of intoxication, often accompanied by fits of laughter: whence the name *Laughing Gas*. Inhaled in larger quantities it produces uncon-

sciousness and insensibility to pain: hence its use as an anæsthetic in dental and other surgical operations.

Chemical.—*Nitrous oxide is almost as good a supporter of combustion as oxygen.* A glowing splint of wood, phosphorus, and highly heated sulphur burn brilliantly in the gas: the burning substances decompose the gas and unite with oxygen, setting nitrogen free—



Hence, in all cases of combustion in nitrous oxide, the combustion is in reality supported by oxygen.

Tests : Distinction with Oxygen.—(1) Nitrous oxide has a peculiar taste and smell, and produces intoxication and insensibility, while oxygen has not these properties.

(2) Nitrous oxide is more soluble in water than oxygen.

(3) Decomposition of nitrous oxide is necessary before it can support combustion. [Feebly burning sulphur (which burns in oxygen) is extinguished in nitrous oxide; sulphur must be highly heated so that it can decompose nitrous oxide and burn in it]. In all cases of combustion in nitrous oxide there is a residue of nitrogen.

(4) The most notable distinction is this:—Oxygen when mixed with nitric oxide produces reddish brown fumes, but no fumes arise when nitrous oxide is added to nitric oxide.

✓ **Composition.**—If a small piece of potassium is heated in a thumb-shaped glass tube containing a known volume of nitrous oxide and standing over mercury (Fig. 37), the potassium burns, uniting with all the oxygen; the volume of nitrogen left is found to be the same as the volume of the original gas. Hence, *nitrous oxide contains its own volume of nitrogen.*

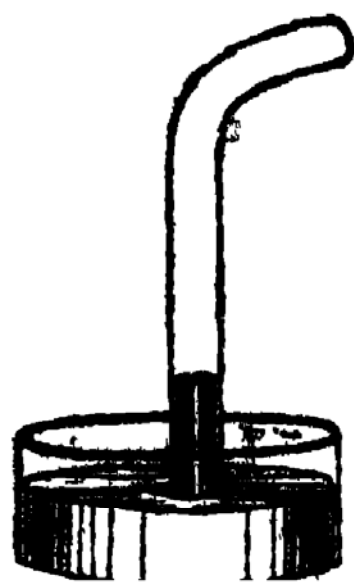


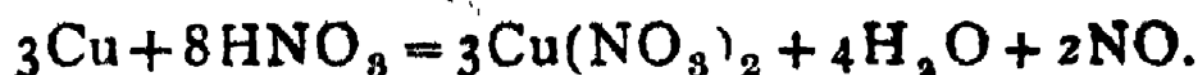
Fig. 37.

The densities of nitrous oxide and nitrogen are 22 and 14 respectively; and it is found that 2 volumes of nitrous oxide contain 2 volumes of nitrogen. Therefore, $2 \times 22 = 44$ parts of nitrous oxide contain $2 \times 14 = 28$ parts of nitrogen and $(44 - 28) = 16$ parts of oxygen. These proportions of the substances correspond to the formula N_2O .

NITROGEN DIOXIDE OR NITRIC OXIDE.

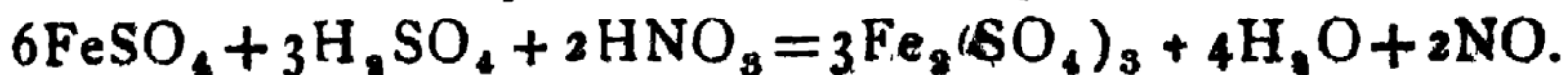
FORMULA NO. MOLECULAR WEIGHT 30. DENSITY 15.

Preparation —(1) Nitric oxide is generally prepared by gently pouring slightly diluted nitric acid over copper turnings contained in a flask furnished with a funnel and a delivery tube (Fig. 13). At first brown fumes will appear: these disappearing, the gas may be collected by displacement of water.



The gas obtained by this method is more or less mixed with nitrogen and nitrous oxide. To purify it, the evolved gas is passed into a cold strong solution of ferrous sulphate by which it is absorbed. On heating the solution, pure nitric oxide is evolved.

(2) Pure nitric oxide may be obtained by gently heating a mixture of ferrous sulphate, nitric acid, sulphuric acid and water.



Properties: Physical.—Nitric oxide is a colourless poisonous gas. It is slightly heavier than air and is almost insoluble in water. It has been liquefied by enormous pressure.

Chemical.—(1) *It combines readily with oxygen forming reddish-brown fumes (of N_2O_3 and NO_2).* Hence the appearance of these fumes in the flask when nitric oxide is prepared.



(2) *It does not ordinarily support combustion.* Thus, a lighted candle or feebly burning phosphorus is extinguished in a jar of the gas. But when strongly burning phosphorus is

introduced, the gas is decomposed, and the phosphorus continues to burn :



(3) A mixture of nitric oxide and vapour of carbon disulphide (obtained by adding a few drops of carbon disulphide to a jar of the gas) burns, when ignited, with a brilliant bluish flame.

Tests.—See above.

Composition.—When a small piece of potassium is heated in a thumb-shaped glass tube containing a measured volume of nitric oxide and standing over mercury, the potassium burns and the volume of nitrogen left is found to be half of the volume of nitric oxide taken.

The densities of nitric oxide and nitrogen are 15 and 14 respectively. Now, 2 volumes of nitric oxide contain 1 volume of nitrogen. Therefore, $2 \times 15 = 30$ parts of nitric oxide contain $1 \times 14 = 14$ parts of nitrogen, and $(30 - 14) = 16$ parts of oxygen. These proportions correspond to the formula NO.

[If the formula of nitric oxide were N_2O_2 , as was formerly believed, then its density would have been 30. But its observed density is 15, and so the correct formula is NO].

NITROGEN TRIOXIDE OR NITROUS ANHYDRIDE.

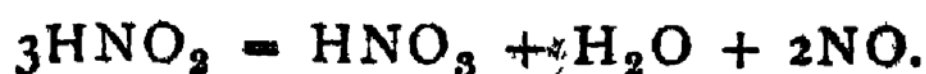
FORMULA N_2O_3 . MOLECULAR WEIGHT 76. DENSITY 38.

Preparation and Properties.—Nitrogen trioxide is prepared (1) by passing through a hot tube a mixture of nitric oxide and oxygen or nitrogen peroxide, or (2) by gently heating arsenious oxide with nitric acid :



The red gas, when cooled to about -20° , condenses to a greenish-blue liquid which vaporises readily into NO and NO_2 . The independent existence of gaseous N_2O_3 is therefore sometimes doubted. Fumes of nitrogen trioxide unite with water to form nitrous acid (HNO_2).

Nitrous Acid and Nitrites.—Nitrous acid is formed by the union of nitrous anhydride with water: $\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2$. This acid is not known to exist in the pure state, and is so very unstable that even in dilute aqueous solution it decomposes readily:



Nitrites are the salts of nitrous acid, and may be formed by passing nitrogen trioxide into a solution of an alkali:



Nitrites are stable compounds, soluble in water, and most of them are decomposed by heat. They are distinguished by the following tests:

(1) When a nitrite is added to an acidulated solution of an iodide, iodine is set free.

(2) Nitrites are decomposed by strong acids, liberating red fumes of nitrogen trioxide—

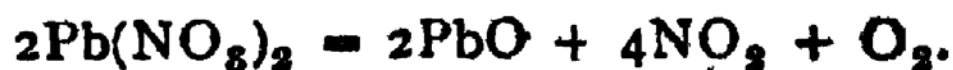


NITROGEN TETROXIDE OR PEROXIDE.

FORMULA NO_2 AND N_2O_4 . MOLECULAR WEIGHT 46 AND 92.

DENSITY 23 AND 46.

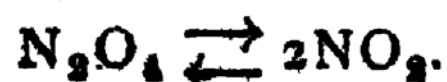
Preparation.—(1) It is prepared by heating dried lead nitrate in a retort, and then conducting the evolved gas into a U-tube immersed in a freezing mixture. The gas condenses at first as a greenish liquid and then as colourless crystals.



(2) It may also be prepared by mixing 4 volumes of nitric oxide and 2 volumes of oxygen, and then passing the red gas through a tube immersed in a freezing mixture.

Properties.—Nitrogen peroxide is poisonous and has a suffocating odour. At -9° it forms colourless crystals, and above 10° it becomes an orange-red liquid which boils at 32° producing brown vapours. The colour of the gas deepens and its density decreases with rise of temperature. The gas

is completely dissociated at 140° , when its density is 23. It is therefore represented by both the formulæ N_2O_4 and NO_2 :



Nitrogen peroxide supports the combustion of strongly burning substances, and readily dissolves in *cold* water to form both nitric and nitrous acids.



When dissolved in excess of warm water, it produces nitric acid and nitric oxide :



NITROGEN PENTOXIDE OR NITRIC ANHYDRIDE.

FORMULA N_2O_5 . MOLECULAR WEIGHT 108.

Preparation.—It is prepared by carefully distilling a mixture of strong nitric acid and phosphorus pentoxide. Nitrogen pentoxide crystallises in the receiver and metaphosphoric acid is left in the retort :



Properties.—It is a white crystalline solid which readily decomposes into oxygen and NO_2 . It rapidly absorbs moisture and dissolves in water to form nitric acid :



University Examination Questions.

1. Give the names and formulæ of the compounds of Nitrogen with Oxygen, and show how they serve to illustrate the Law of Multiple Proportion [C. 92].

How may the oxides of nitrogen be prepared? What occurs when they are brought in contact with water? [A. 05].

Describe the methods, direct or indirect, by which each of the oxides of nitrogen can be prepared from nitric acid [A. 1910]. Starting with nitric acid, how would you prepare nitric oxide and nitrogen peroxide? [C. 1910].

2. Describe carefully making a sketch of the apparatus you would use to prepare and collect nitrous oxide gas [C. 05 ; A. 02, 12].

State the chief properties of the gas and the manner in which it is distinguished from oxygen. [A. 02.]

What volume of nitrous oxide, at 15°C . and 770 mm. pressure can I get by decomposing 400 grammes of ammonium nitrate? [A. 1900].

How can you determine the composition of nitrous oxide? [A. 1911, 12]. Describe an experiment to prove that *nitrous oxide* contains its own volume of nitrogen, and hence deduce its molecular formula, given its density to be 22. [C. 1912, 14.]

3. How would you prepare pure nitrogen dioxide? Describe its chief properties. Describe the experiment made to determine its composition. What is its formula, and why is it given? [C. 08, 15]

How would you prepare and fill a jar with nitric oxide gas; illustrate your answer by a sketch [C. 97, 03; A. 03]. State the chief properties of the gas [C. 97]. What is the result of mixing air with this gas, and then shaking up with water? Give equations in each case. [C. 03; A. 03].

Compare the properties of nitrogen monoxide and nitrogen dioxide. [C. 1914.]

If the oxygen be removed from 10 cubic centimetres of nitric oxide, what volume of nitrogen will remain? [C. 97].

4. Give one method for the preparation of Nitrous Anhydride. Can we prepare Nitrous Acid from it? If so, how? [A. 09].

CHAPTER XXII.

CARBON AND ITS COMPOUNDS.

SECTION I.

✓ CARBON.

SYMBOL C. ATOMIC WEIGHT 12.

Different Forms of Carbon.—Carbon occurs in three different forms, *viz.*, Diamond, Graphite, and Amorphous Carbon. The first two are pure carbon and have *crystalline* structures, while the third (of which there are many varieties, all of which are more or less impure) is non-crystalline. The former are found in nature in the free state, the latter is produced from organic compounds (*i.e.* substances of animal and vegetable origin) and is also found in the natural substances coal, chalk, marble, limestone, &c. Wood-charcoal, bone-black, coke, lampblack, soot, &c. are all varieties of amorphous carbon.

✓ That diamond, graphite, charcoal &c. are different *allotropic modifications* of the same element Carbon, may be shown both from their physical and chemical properties :—

(1) All of them are tasteless and inodorous ; they are insoluble in water or in any liquid, and can stand heat to a high degree without being melted.

(2) When burnt in air, all of them yield only carbon dioxide ; and if equal quantities of diamond, graphite, and pure charcoal be burnt, the quantity of carbon dioxide produced in each case will be the same. Conversely, knowing the composition of carbon dioxide, if we can calculate how much carbon is contained in a given quantity of carbon dioxide (obtained by burning diamond, graphite, or charcoal), we will find that the calculated weight of carbon is equal to the actual weight of the diamond or graphite or charcoal used.

Formation and Physical Properties of Carbon.—

Diamond.—It is the purest form of carbon, found in India, South Africa, Australia, Brazil, and the United States. It is a crystalline substance with great brilliance and lustre, and is colourless when pure. It is the hardest substance known, and its specific gravity is nearly 3.5. It does not conduct heat or electricity, and burns at an exceedingly high temperature. The origin of diamond is still unknown. Moissan has shown its artificial formation by dissolving carbon in molten iron (at a temperature above 3000°) and then suddenly cooling the whole mass by plunging it into water or molten lead. On dissolving the iron in acid, minute crystals of diamond are found in the residue.

Graphite.—It is found in India, Siberia, and California. It is now manufactured by heating in an electric furnace a mixture of 97 parts of charcoal and 3 parts of iron. Graphite is a smooth, shining, grayish-black, crystalline substance. Outwardly it resembles the metal lead, and is therefore also called *plumbago* or *black-lead*. It is so soft that it marks paper ; its specific gravity is nearly 2.2. It is a good conductor of heat and electricity, and burns when strongly heated.

Charcoal, &c.—None of the varieties of amorphous carbon are pure carbon. They are generally obtained by the destructive distillation of organic substances, or by burning them in a limited supply of oxygen. Thus, wood-charcoal is obtained by firing wood piled into stacks and covered with turf. Similarly, coke and gas-carbon are obtained as residues in the destructive distillation of coal. Bone-black (also called 'ivory-black' and 'animal charcoal') is prepared by heating bones in closed retorts, and lamp-black or soot is obtained from burning oils. The specific gravity of amorphous carbon varies from 1.5 to 2.3. All the varieties (except gas-carbon) are bad conductors of heat and electricity. Charcoal being porous absorbs gases and withdraws colouring-matters from liquid solutions.

Coal.—It is a very impure form of carbon. Coal is the product of the decay of vegetable-matters of past ages, in the absence of free air and under great pressure of the earth. There are principally two varieties of coal, *viz.*, (1) soft or bituminous, and (2) hard or anthracite. Soft coal burns with a smoky flame and is used for the manufacture of coal-gas. Hard coal burns with great heat but little smoke or flame, and is used as steam-coal. Hard coal contains more carbon than soft coal does.

Chemical Properties of Carbon.—The several forms of carbon, though differing widely in their physical properties, are chemically the same element. At ordinary temperatures carbon is inactive, but at very high temperatures it combines with oxygen, sulphur, iron, and some other elements. Carbon burns in air or oxygen producing carbon dioxide. It is a great reducing agent: when an oxide of a metal (*e.g.* copper oxide) is heated with carbon, the oxygen is abstracted by carbon and the metal is set free—



Uses of Carbon.—The chief uses of carbon are these:

- **Of Diamond.**—It is valued as a gem and is used for cutting glass, rock-boring, grinding and polishing hard substances.

Of Graphite.—It is used for the manufacture of the so-called lead-pencils and of crucibles, for making anodes in electrolytic processes, for polishing gunpowder and protecting iron-work from rusting, and as a dry lubricant.

Of Charcoal, &c.—Wood-charcoal and coke are used as fuel and as reducing agents in metallurgical operations. Wood-charcoal is also used in water-filters, for gunpowder, and as a disinfectant. Bone-black is used in sugar-refining, lampblack for printer's ink and black paint, gas-carbon in voltaic batteries and the arc-light.

University Examination Questions.

1. In what forms is pure carbon found in nature? Describe their distinguishing properties [C. 99].
2. Name the allotropic modifications of carbon, and give reasons why they are to be regarded as such [A. 1915]. The diamond, graphite, and charcoal are said to be allotropic forms of one element. Give reasons for this statement [C. 06].
3. Mention the natural and artificial forms of carbon. Compare their properties, and indicate their uses in the arts and in the laboratory. [C. 1913]. Compare the allotropic forms of carbon [C. 1900 ; A. 94, 98.]. Give a short description of the allotropic modifications of carbon, and mention their chief uses [C. 09]. Name the amorphous forms of carbon. How are they obtained? Mention their important uses in the arts and manufactures [C. 1911].

SECTION II.

OXIDIES OF CARBON.

✓ CARBON DIOXIDE or CARBONIC ACID GAS.

FORMULA CO_2 . MOLECULAR WEIGHT 44. DENSITY 22.

Occurrence.—It occurs in the free state in the air (especially in the vicinity of volcanoes) and in many mineral waters. In combination, it is abundantly found in chalk, marble, limestone, coral, &c. Carbon dioxide is given out by animals with their breath, and it is produced whenever carbon and its compounds burn or naturally decay in a sufficient supply of air or oxygen.

Preparation.—The modes of preparation are these :

I. By adding an acid to a carbonate. For laboratory pur-

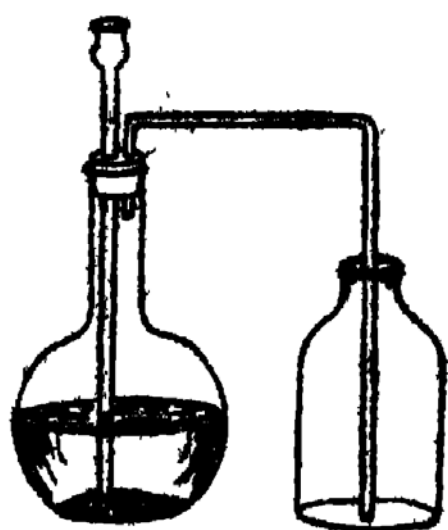


Fig. 38.

poses, fragments of calcium carbonate (*i. e.* chalk, marble, or limestone) are placed in a flask or a two-necked bottle which is furnished with a thistle-funnel and a delivery tube ; on the addition of hydrochloric acid through the funnel tube, the gas is evolved rapidly. It is collected by downward displacement (or by displacement of water).



NOTE.—In preparing the gas we may use sulphuric acid instead of hydrochloric acid, $[\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2]$. But in this case *powdered* chalk must be used, and the mixture must be stirred constantly. For if lumps of CaCO_3 be employed, the insoluble calcium sulphate (CaSO_4) will soon form a coating on them, and thus put an end to the reaction by preventing the acid to come in contact with the carbonate.

II. By strongly heating calcium carbonate.



III. By burning carbon in a free supply of air or oxygen, or by decomposing organic matters. For example, cane-sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is converted into alcohol and carbon dioxide by fermentation :

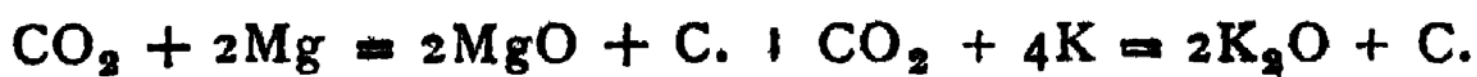


Properties : Physical.—Carbon dioxide is a colourless gas, having a slight acid taste and smell. It is not poisonous, but it does not support respiration ; when inhaled in excess it produces suffocation and may even cause death : hence the name 'choke-damp' given to it by miners. It is nearly $1\frac{1}{2}$ times heavier than air, and can be poured (like a liquid) from one vessel into another. By cold and pressure it can be easily changed into the liquid and solid states.

✓ *Carbon dioxide is soluble in water ; hence its use in the preparation of aerated waters : the so-called 'soda water' being nothing more than water charged with carbon dioxide under*

pressure. Its solution in water is called Carbonic Acid (H_2CO_3); hence carbon dioxide is also known as *carbonic acid gas* or *carbonic anhydride*.

Chemical.—Carbon dioxide does not burn; nor does it ordinarily support combustion. As it has great power of extinguishing flame, it is conveniently used as a 'fire-extinguisher.' But some metals having a great affinity for oxygen burn in it: thus, when a burning magnesium wire is introduced into the gas, or when potassium is heated in it, the metal continues to burn—



Carbon dioxide unites with alkalis to form carbonates. Thus, when it is passed into a clear solution of lime-water (calcium hydrate, CaH_2O_2), the liquid at once becomes turbid, owing to the formation of calcium carbonate which is insoluble in water—



Test.—Carbon dioxide is readily distinguished by its property of turning limewater milky. (See below).

Composition.—The composition of carbon dioxide may be shown by means of a U-shaped eudiometer, open at one end and having a bulb at the other. The bulb has a stopper through which pass two copper wires, one of which carries a small porcelain boat. A piece of pure carbon is placed in the boat and a platinum wire is connected with the copper wires and made to touch the carbon. The tube is first filled with mercury, oxygen is then introduced into the bulb and the mercury is brought to the same level in the two limbs of the tube. On passing an electric current through the wires, the carbon is ignited and unites with oxygen to form carbon dioxide. When the apparatus has cooled, it will be found that the volume of carbon dioxide is the same as the original volume of oxygen. Hence, *carbon dioxide contains its own volume of oxygen*.

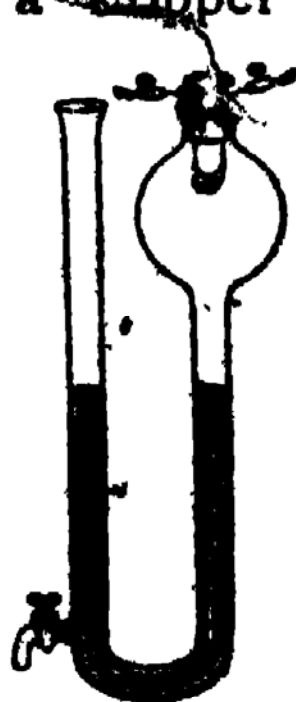


Fig. 39.

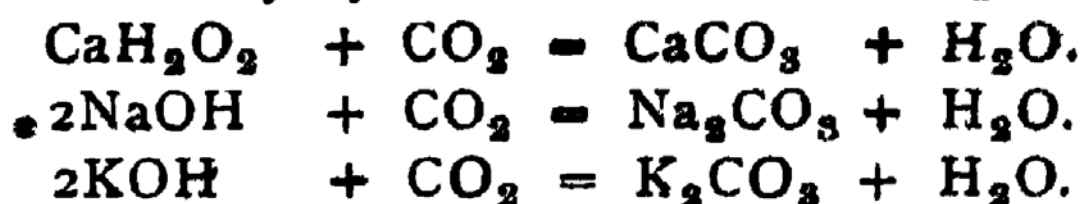


The formula CO_2 .—The densities of carbon dioxide and oxygen are 22 and 16 respectively, and it is seen that 2 volumes of carbon dioxide contain 2 volumes of oxygen. Therefore $2 \times 22 = 44$ parts of carbon dioxide contain $2 \times 16 = 32$ parts of oxygen and $(44 - 32) = 12$ parts of carbon. Hence the formula of carbon dioxide is CO_2 .

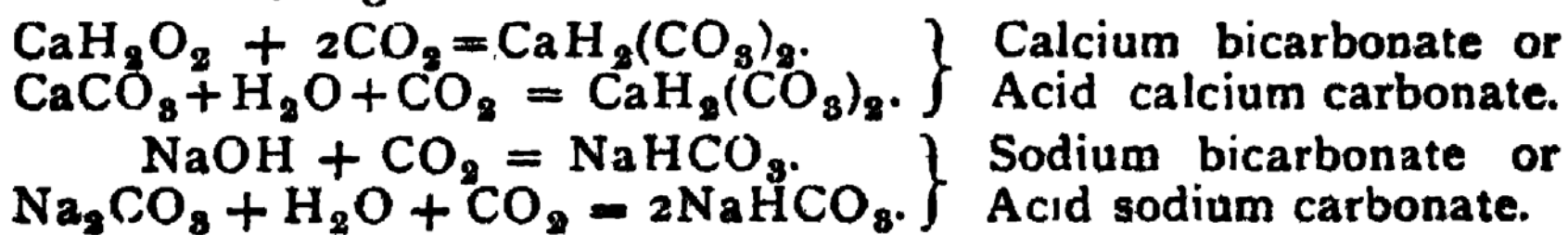
CARBONIC ACID AND CARBONATES.

Carbonic Acid, H_2CO_3 , is formed when a solution of carbon dioxide in water is exposed to pressure for sometime [$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$]. Carbonic acid is a very unstable compound, being readily decomposed by heat into CO_2 and H_2O . It has only feeble acid properties, changing blue litmus to a port-wine red colour. Carbonic acid is dibasic, forming two series of salts which are stable compounds.

Carbonates are the salts of carbonic acid. They fall into two groups, *viz.*, normal carbonates and acid carbonates (or bicarbonates). The former are produced when carbon dioxide is absorbed by hydroxides of metals, *e. g.*—



The latter are produced when carbon dioxide is used in excess, or when it is passed into aqueous solutions of normal carbonates, *e. g.*—



Many normal carbonates are insoluble in water, while the corresponding bicarbonates are soluble. Thus, when carbon dioxide is passed into limewater (CaH_2O_2), the liquid becomes turbid owing to the formation of chalk (CaCO_3) which being insoluble is precipitated. But when more carbon dioxide is passed through the turbid solution, the liquid again

becomes clear owing to the formation of bicarbonate of lime $[\text{CaH}_2(\text{CO}_3)_2]$ which is soluble. Hence, it is sometimes said that *calcium carbonate is soluble in excess of carbonic acid*. When a solution of calcium bicarbonate is heated it is decomposed, and the water becomes once more turbid owing to the precipitation of the insoluble carbonate—



This fact is illustrated in removing the temporary hardness of water. Addition of fresh lime-water to the solution produces almost the same result—



Carbonates are decomposed by acids with the liberation of carbon dioxide.

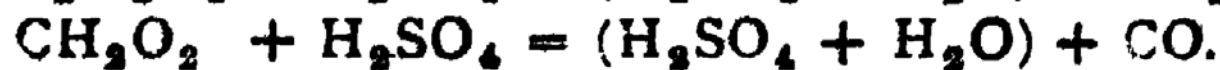
CARBON MONOXIDE OR CARBONIC OXIDE.

FORMULA CO. MOLECULAR WEIGHT 28. DENSITY 14.

Occurrence.—This gas is not found in the free state in nature, but is produced when carbon burns in an insufficient supply of oxygen.

Preparation.—The methods of preparation are these :

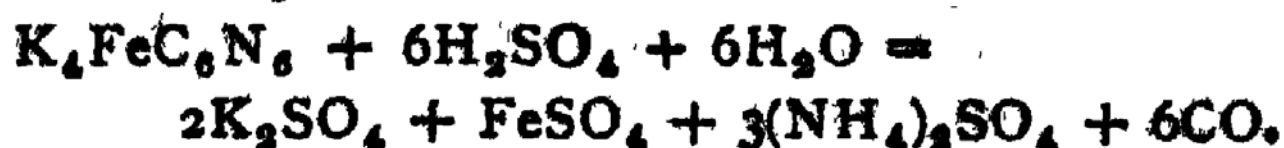
(1) *By heating oxalic or formic acid with strong sulphuric acid.* In the laboratory, oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) or formic acid (CH_2O_2) is heated with strong sulphuric acid in a flask [Fig. 14]; owing to its great affinity for water, H_2SO_4 decomposes the organic compounds by withdrawing water from them—



In the first case, in which a mixture of CO_2 and CO is evolved, the mixed gases are passed through a wash-bottle containing a solution of caustic soda or caustic potash which absorbs CO_2 . Thus CO is set free and is collected by displacement of water.

In the latter case, sodium formate (NaCHO_2) may be used instead of formic acid.

(2) *By heating a mixture of potassium ferrocyanide and concentrated sulphuric acid—*



(3) *By passing carbon dioxide over red-hot carbon or iron contained in a tube—*



(4) *By strongly heating carbon or iron with chalk—*



(5) *By passing steam over highly heated carbon contained in a tube.* By this means a mixture of hydrogen and carbon monoxide is produced: this mixture of the two inflammable gases being called water gas—



• **Properties: Physical.**—Carbon monoxide is a colourless, tasteless, and almost inodorous gas. It is very slightly soluble in water, and can be liquefied only with great difficulty. *It is extremely poisonous*, causing giddiness, insensibility, and death when inhaled. Hence the great necessity of keeping our rooms well ventilated when there is fire burning within.

✓ **Chemical.**—(1) *It is inflammable*, and burns with a peculiar lambent blue flame, forming carbon dioxide.



(2) At high temperatures, *carbon monoxide acts as a good reducing agent*. Thus when the gas is passed through red-hot copper oxide, metallic copper and carbon dioxide are produced. $[\text{CuO} + \text{CO} = \text{Cu} + \text{CO}_2]$. Hence the use of carbon monoxide in reducing the ores of metals.

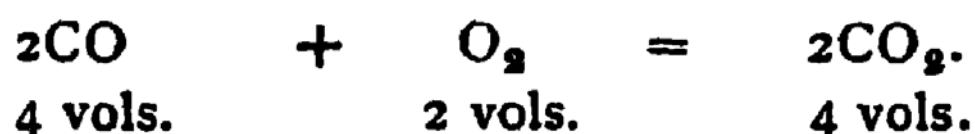
(3) When a mixture of carbon monoxide and chlorine is exposed to sunlight, carbonyl chloride (COCl_2), known as *phosgene gas*, is formed.

(4) At a high temperature carbon monoxide unites with caustic potash to produce potassium formate (KCHO_2).

Tests.—(1) Carbon monoxide burns with a pale blue flame forming CO_2 which turns limewater milky.

(2) It is separated from other gases by a solution of cuprous chloride which absorbs it.

Composition.—When a moist mixture of nearly equal volumes of carbon monoxide and oxygen is introduced in a eudiometer and exploded, we get a mixture of carbon dioxide and oxygen. On absorbing the carbon dioxide with caustic soda or potash, and measuring the volume of the residual oxygen under the same temperature and pressure, it is found that 100 volumes of carbon monoxide unite with 50 volumes of oxygen to form 100 volumes of carbon dioxide. But as 100 volumes of carbon dioxide contain 100 volumes of oxygen, the remaining 50 volumes of oxygen must have been contained in 100 volumes of carbon monoxide. That is, *carbon monoxide contains half its volume of oxygen.*



Its formula.—The densities of carbon monoxide and oxygen being 14 and 16 respectively, it follows that $2 \times 14 = 28$ parts of carbon monoxide contain $1 \times 16 = 16$ parts of oxygen and $(28 - 16) = 12$ parts of carbon. Hence, the formula of carbon monoxide is CO .

University Examination Questions.

I.

1. Write an account of the substance Carbon dioxide [A. 93]. Write an essay on 'carbonic acid gas' giving all and any information you have derived from your own experiments in the laboratory [C. 09].

2. Describe the method of preparing and collecting carbon dioxide, and sketch the apparatus you would use for the purpose [C. 98]. Describe two methods of preparing carbon dioxide [C. 93; A. 14].

What volume of gas is produced by the action of a gram of

hydrochloric acid gas upon two grams of marble, if the gas is measured at 136° C. and 380 mm. pressure? [A. 06].

What weight of calcium carbonate must be decomposed by hydrochloric acid to produce a quantity of carbon dioxide that will suffice for the conversion of 30 grammes of caustic soda into sodium carbonate? ($\text{Ca} = 40$, $\text{Na} = 23$). [C. 03].

3. You are given a number of cylinders of carbon dioxide gas. Describe the experiments you would perform to illustrate the chief chemical and physical properties of the gas. [C. 1915]. Describe, with due attention to practical details, experiments with carbon dioxide to show (a) its density, (b) its solubility in water, (c) its action on limewater. [C. 1910]. Describe experiments proving that carbon dioxide is heavier than the same volume of air. How would you show that water is able to dissolve CO_2 ? [C. 05].

4. Give full instructions for performing the experiment by which it could be demonstrated that carbon dioxide contains its own volume of oxygen. [A. 14]. How would you prove that CO_2 is the formula for carbon dioxide? [C. 99 ; A. 03.]

II.

1. How would you prepare a few cylinders of carbon monoxide gas? Sketch the apparatus you would employ. What experiments would you make to illustrate the principal properties of the gas? [C. 1913 ; A. 95].

Describe the method of preparation of carbon monoxide from carbon dioxide and carbon. What volume of carbon monoxide can be obtained theoretically from 100 litres of carbon dioxide, both measured under standard conditions of temperature and pressure? [C. 01.]

How does water-gas differ from steam? [C. 98].

2. State how you would distinguish physically and chemically between carbon dioxide and carbon monoxide [C. 93.]

3. How would you separate CO from CO_2 in a mixture of the two gases? One litre of such a gas-mixture is found to give 1600 c.c. of CO, both measured under the same conditions. Calculate the composition by volume of the gas-mixture. [C. 14].

SECTION III.

HYDROCARBONS.

Hydrocarbons are the compounds of carbon with hydrogen. Their number is exceedingly large, and they form what is called a *homologous series*, the consecutive members differing from each other by CH_2 . Hydrocarbons form the study of Organic Chemistry; but three compounds, *viz.*, CH_4 , C_2H_2 , and C_2H_4 are the representatives of three homologous series, and being the more important are treated of in Inorganic Chemistry. The hydrocarbons are not chemically active; all of them burn in air, and when passed through a white-hot tube they split up into hydrogen and other hydrocarbons.

✓ MARSH GAS OR METHANE.

(*Light Carburetted Hydrogen.*)

FORMULA CH_4 . MOLECULAR WEIGHT 16. DENSITY 8.

Occurrence.—It is formed by the decomposition of vegetable matter (*e. g.* leaves of plants) in absence of air, and is therefore found in the free state in marshes (whence the name of the gas) and in the bottom of stagnant ponds. It also occurs largely in coal mines and oil pits, and is contained in coal-gas, petroleum, &c.

Preparation.—Marsh gas is prepared by strongly heating a mixture of sodium acetate and caustic soda. In the laboratory, dried sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) is mixed with an excess of soda-lime, and the mixture is strongly heated in an iron tube or a copper retort. The gas is collected over water (Fig. 14).



[*Soda-lime* is quicklime slaked with a solution of caustic soda. As strong heat is required for the above reaction, quicklime is added to prevent the mixture from fusing].

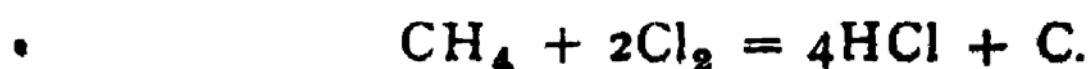
Properties: Physical.—Marsh gas is colourless, tasteless and inodorous. It is half as light as air and is very slightly soluble in water.

Chemical.—It is highly combustible and burns with a non-luminous pale flame. A mixture of marsh gas and air (or oxygen) explodes violently on ignition. These explosions being frequent in coal mines, pit-men call the gas 'fire-damp'. The result of its combustion or explosion is carbon dioxide and water—



This resulting CO_2 is, by virtue of its suffocating property, called by miners 'choke-damp' or 'after-damp.'

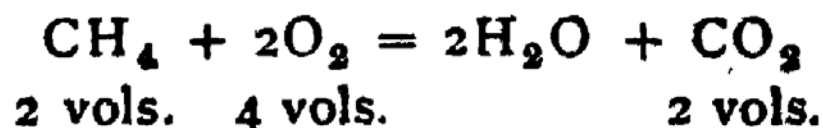
Marsh gas is decomposed by chlorine. When a mixture of chlorine and marsh gas is exposed to bright sunshine, clouds of hydrochloric acid are formed and carbon is deposited on the sides of the vessel—



But usually chlorine acts on marsh gas to produce hydrochloric acid and a series of carbon compounds (the nature of which depends on the quantity of chlorine used).

Tests — See chemical properties above.

Composition.—A known volume (say, 2 volumes) of marsh gas and thrice as much oxygen are introduced in a eudiometer, and the mixture is exploded. On absorbing the residual carbon dioxide with caustic potash, we find that 2 volumes of marsh gas require 4 volumes of oxygen to produce 2 volumes of carbon dioxide. Out of these 4 volumes of oxygen, 2 volumes go to form the carbon dioxide, and the remaining 2 volumes must unite with 4 volumes of hydrogen to form water. These 4 volumes of hydrogen must therefore be contained in 2 volumes of marsh gas.



Now, as the densities of marsh gas and hydrogen are 8 and 1 respectively, 16 parts of marsh gas contain 3 parts of hydrogen and $(16 - 4) = 12$ parts of carbon. Hence its formula is CH_4 .

[The composition of ethylene and of acetylene may be determined by similar methods].

ETHYLENE OR OLEFIANT GAS.

*(Heavy Curburetted Hydrogen).*FORMULA C_2H_4 . MOLECULAR WEIGHT 28. DENSITY 14.

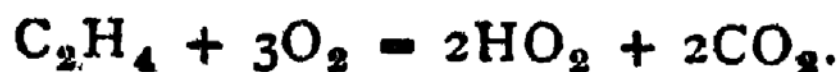
Occurrence.—Ethylene occurs in coal-gas, the luminosity of which is due chiefly to its presence.

Preparation.—It is prepared by heating in a flask a mixture of alcohol (C_2H_5O) and strong sulphuric acid. [A quantity of sand is thrown into the flask to prevent the liquid frothing up. The acid abstracts the elements of water from alcohol, and ethylene is liberated. The gas is purified by being passed through a solution of caustic soda, and is then collected by displacement of water.



Properties: Physical.—Ethylene is a colourless gas having a sweetish ethereal smell. It is almost as heavy as air.

Chemical.—Ethylene burns with a highly luminous smoky flame. Its mixture with air or oxygen explodes violently on ignition. The product of combustion and explosion is carbon dioxide and water—



Ethylene combines with an equal volume of chlorine to form an oily liquid ($C_2H_4Cl_2$), called ethylene dichloride or *Dutch liquid*; hence the name 'olefiant gas.' When, however, ethylene is mixed with twice its volume of chlorine and the mixture is ignited, ethylene is decomposed—



Ethylene is absorbed by strong sulphuric acid.

Tests.—See above.

ACETYLENE.

FORMULA C_2H_2 . MOLECULAR WEIGHT 26. DENSITY 13.

Occurrence.—Acetylene occurs in small quantities in coal-gas. It is formed when coal-gas or methane burns in a

limited supply of oxygen, *e.g.*, when a Bunsen burner burns at the base of the tube.

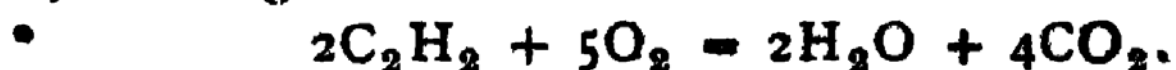
Preparation.—(1) It is prepared by the action of water on calcium carbide :



(2) The gas may be synthetically prepared by passing an electric current through two carbon electrodes enclosed in a glass globe filled with hydrogen.

Properties : Physical.—It is a colourless gas having a disagreeable smell. It is more soluble in water than either methane or ethylene.

Chemical.—*It burns with a bright but smoky luminous flame, forming carbon dioxide and water :*



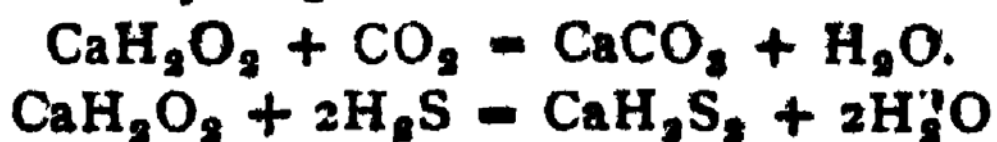
When it is passed into an ammoniacal solution of cuprous chloride, a red precipitate (known as *copper acetylene*) is formed. Nascent hydrogen converts acetylene into ethylene.

Test.—See above.

Uses.—Acetylene is used as an illuminant.

COAL GAS.

Coal-gas is a mixture of many compound substances, produced by the destructive distillation of coal. When coal is heated without contact of air, it yields (a) coke and (b) three volatile products, *viz.*, (1) coal tar, (2) ammoniacal liquor, and (3) coal-gas. For the manufacture of coal-gas, bituminous coal is strongly heated in iron retorts : the volatile products being conducted through condensers and tanks, the tarry matter and ammoniacal watery liquid remain behind and coal-gas passes off. Before being collected over water in a gas-holder, the gas is led into purifying chambers where it slowly passes over slaked lime (CaH_2O_2) spread on trays, and is thus freed from such impurities as carbon dioxide and sulphuretted hydrogen :



Coal-gas consists of several gases which fall into three groups, *vis.*, Illuminants, Diluents, and Impurities. The Illuminants are hydrocarbons which impart light to the coal-gas flame, and the Diluents give out heat when burnt and dilute down the hydrocarbons which would otherwise burn with too smoky a flame. The average amounts of the constituents in 100 volumes of coal-gas are the following :

Diluents.—Hydrogen, Marshgas, Carbon monoxide...91 per cent.

Illuminants.—Ethylene, Acetylene, Benzene, &c. ... 5 „ „

Impurities.—Nitrogen, Carbon disulphide, &c. ... 4 „ „

University Examination Questions.

I.

1. What is Methane and where does it occur in nature? How is it ordinarily prepared in the class? Describe its properties [C. 08; A. 15], and justify its formula [C. 08.] How would you distinguish it from the other hydrocarbons known to you? [A. 15].

2. How is Methane prepared in the laboratory? Give an account of the experiments you would perform to demonstrate three of its important properties. [C. 14].

3. How may marsh gas be prepared? [A. 09, 12]. You often hear of explosions taking place in coal-mines. What is this due to? Are they preventible, and how? [C. 1911]. Describe fully how you would determine the composition and molecular formula of marsh gas [C. 1912; A. 02, 12].

4. 25 c.c. of Marsh gas at N. T. P. are mixed with 300 c.c. of air at 27° C. and 750 mm. pressure, and the mixture is exploded by electric sparks. Find the volume of the residual gas at 17° C. and 750 mm. Air contains 20% of oxygen and 80% of nitrogen (by volume). [C. 1916].

II.

Describe fully the preparation and properties of ethylene gas [C. 04, 06; A. 04, 13]. Explain how you would distinguish it from marsh gas [C. 06].

III.

1. How is acetylene gas prepared? Give equations. Describe its properties, and give its tests and uses. [C. 1916].

2. Describe the preparation and properties of acetylene gas [A. 01]. Describe the preparation of ethylene and acetylene. How would you distinguish between the two gases [A. 1911].

3. Calculate the weight of CO_2 produced by the complete combustion of 15 litres of Acetylene [A. 09].

IV.

How is coal-gas prepared and purified? Give equations to show the reactions involved in the purification [A. 1912]

CHAPTER XXIII.

THE HALOGENS AND THEIR COMPOUNDS.

The Halogens—The four elements Fluorine, Chlorine, Bromine, and Iodine constitute a group known as the *halogens*. These elements (and their compounds) have strong resemblances among themselves, and they exhibit a gradation in their properties with increasing atomic weight. They may be compared as follows.

Their Physical Features.—(1) The atomic weights of Fluorine, Chlorine, Bromine, and Iodine are respectively 19, 35.5, 80, and 127.

(2) The first two are gases at ordinary temperatures, bromine is a liquid, and iodine is a solid. Their volatility decreases as we pass from fluorine to iodine.

(3) In their colour fluorine is pale yellow, chlorine is greenish yellow, bromine is reddish brown, and iodine is violet-black.

(4) All of them have characteristic pungent odours.

Their Chemical Features.—(1) They combine with hydrogen alone to form colourless fuming acids.

(2) They combine with metals to produce similar salts: owing to the resemblance of their sodium and potassium salts with sea-salt the name *halogen* (—‘salt-producer’) has been given to them.

(3) In their union with hydrogen and metals, the halogens are monovalent and their chemical activity decreases as the atomic weight increases. Thus, in these compounds, chlorine displaces both bromine and iodine, and bromine displaces iodine, but not *vice versa*.

(4) Their affinity for oxygen, on the other hand, increases with the increase of atomic weight. Thus, the oxygen compounds of iodine are the most stable, and iodine displaces the other halogens from their oxygen compounds.

SECTION I.

Chlorine and its Compounds.

CHLORINE.

ATOMIC WEIGHT 35.5. DENSITY 3.2. MOLECULAR FORMULA Cl_2 .

Occurrence.—Chlorine does not occur in the free state in nature, but is largely found in combination with metals specially as sodium chloride or common salt.

Preparation.—In the laboratory the gas is prepared by either of the following two methods :

(a) Small lumps of manganese dioxide and strong hydrochloric acid are gently heated in a flask : the chlorine gas which is evolved is purified and dried by being passed through two wash-bottles containing water and sulphuric acid respectively, and is collected in a jar by downward displacement of air.

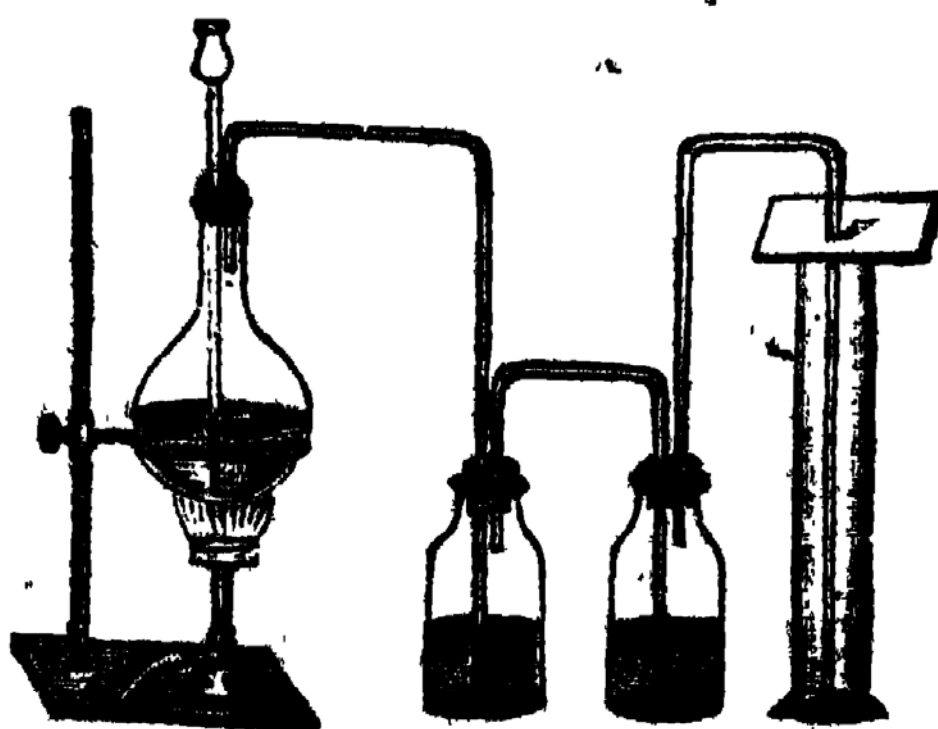


Fig. 40.



(b) A mixture of common salt, manganese dioxide, and sulphuric acid is heated in a flask, and the evolved gas is col-

lected as above described. The reaction may be expressed in two ways :



2. Chlorine is also evolved when hydrochloric acid is acted upon by such oxidizing agents as lead dioxide, potassium bichromate, potassium permanganate, and nitric acid.

3. Chlorine is produced by the action of an acid on bleaching-powder (CaOCl_2) :



4. Chlorine is also obtained by the electrolysis of hydrochloric acid or of a solution of common salt.



Manufacture.—Chlorine is prepared for commercial purposes by the following methods :

Weldon's process.—In this process chlorine is first prepared from manganese dioxide and hydrochloric acid, and the residual manganese chloride is treated with slaked lime and air, with the formation of a compound (called Weldon's mud) which acts on hydrochloric acid liberating chlorine again.

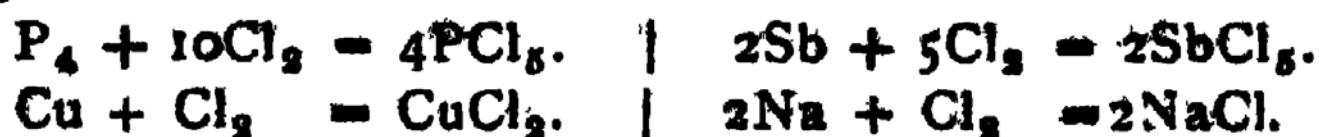
Deacon's process.—In this method air and hydrochloric acid are passed over heated bricks saturated with a solution of copper sulphate (which serves as a catalyzer). This results in the decomposition of hydrochloric acid, chlorine being set free—



Electrolytic process.—See preparation of sodium and caustic soda, Chap. XXVIII.

Properties: Physical.—Chlorine is a gas of a greenish-yellow colour, as its name implies. It has a peculiar pungent suffocating odour and it is poisonous to inhale; hence, all experiments with chlorine are performed in the open air or in a 'draught chamber.' Chlorine is nearly $2\frac{1}{2}$ times as heavy as air, and is soluble in water (the solution being called *chlorine water*). It can be easily liquefied.

Chemical.— 1. *Chlorine supports combustion, and readily combines with phosphorus and many finely divided metals, with the formation of chlorides.* Thus, a piece of phosphorus, powdered antimony, and thin leaves of copper when introduced into chlorine, at once take fire: and heated sodium burns brightly in it—



2. *Chlorine has great attraction for hydrogen.* It readily unites with free hydrogen and abstracts it from many hydrocarbons; thus—

(a) A mixture of hydrogen and chlorine explodes when exposed to bright sunlight, hydrochloric acid gas being formed.



(b) A burning jet of hydrogen continues to burn in a jar of chlorine, and fumes of HCl are formed.

(c) A lighted taper continues to burn when inserted in a jar of chlorine: HCl is formed, and the carbon of the taper produces copious smoke.

(d) If a piece of filter-paper is moistened with turpentine ($\text{C}_{10}\text{H}_{16}$) and plunged into a jar of chlorine, the turpentine takes fire and clouds of HCl and soot (carbon) are evolved.



(e) Water is slowly decomposed by chlorine under the influence of sunlight.



3. *Chlorine bleaches vegetable colouring matters in the presence of moisture or water.* Thus, when a piece of red cloth is partly moistened with water and then placed in a jar of chlorine, the moist portion is decolorized, while the dry portion remains unchanged. Similarly, moist red flowers become white or colourless when introduced into chlorine.

Chlorine bleaches vegetable colouring matters (e.g. indigo, litmus, magenta, writing ink, &c.) ; but dry chlorine does not attack dry coloured substances. The bleaching action of

chlorine is due to the fact that chlorine combines with the hydrogen of water, and the liberated oxygen (in its nascent state) attacks the colouring matters. For industrial uses, chlorine is kept in the form of 'chloride of lime' (CaOCl_2) known as 'bleaching power.' (See Chap. XXIX).

4. *Chlorine is a valuable disinfectant.* Sick-rooms, drains, &c. are disinfected with a solution of bleaching powder. By virtue of its affinity for hydrogen, chlorine decomposes bad-smelling gases. For example, the action of chlorine on sulphuretted hydrogen is to produce HCl and precipitate sulphur.



5. When chlorine is passed through a cold solution of an alkali, we get a mixture of a chloride and a hypochlorite; but when it is passed through a warm and strong alkali solution, a mixture of a chloride and a chlorate is produced. Thus—



Tests.—(1) Chlorine is known by its characteristic colour, odour and bleaching properties.

(2) Chlorine liberates iodine from potassium iodide; hence iodised starch-paper is turned blue by chlorine—



Uses.—Chlorine is used as a disinfectant and bleaching-agent. (See above).

HYDROCHLORIC ACID OR HYDROGEN CHLORIDE.

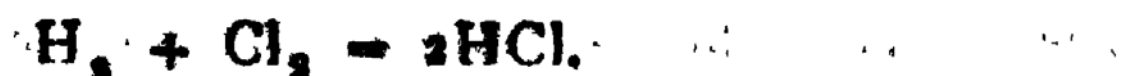
(Muriatic Acid, Spirit of Salt).

FORMULA HCl . MOLECULAR WEIGHT 36.5. DENSITY 1.25.

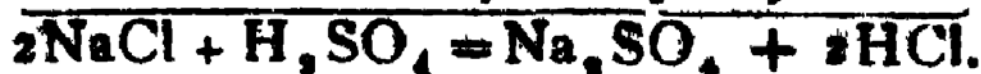
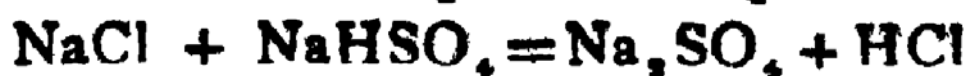
Occurrence.—Hydrochloric acid gas is evolved during volcanic eruptions. The salts of the acid occur plentifully.

Preparation.—(1) Hydrochloric acid gas (i.e., hydrogen chloride) may be synthetically prepared by exposing to daylight a mixture of hydrogen and chlorine. When the mixture is kept in the dark, no action takes place; but if the mixture is exposed

to bright sunshine or is ignited, the gases at once combine with an explosion.



(2) In the laboratory, hydrochloric acid gas is prepared by heating in a flask a mixture of common salt and sulphuric acid. [The apparatus employed is that used in the preparation of chlorine]. The evolved gas is dried by passing it through one or more wash-bottles containing sulphuric acid, and is then collected over mercury or by downward displacement of air. The reaction takes place in two stages, a very high temperature being required for the second reaction—



Manufacture.—Hydrochloric acid (in aqueous solution) is obtained in large quantities in the above way, as a bye-product in the 'salt-cake process' of alkali manufacture (See Chap. XXVIII). The hydrochloric acid gas produced in the furnace is conveyed to condensing towers (filled with bricks or coke) where the gas is absorbed by a stream of water.

Properties: Physical.—Hydrogen chloride is a colourless gas with a pungent choking smell. The gas can be liquefied by pressure only. *It is extremely soluble in water*; hence it fumes in contact with moist air (the clouds being the solution of HCl in the aqueous vapour of the air). The solubility of the gas may be illustrated, as in the case of ammonia, by the Fountain Experiment. Its aqueous solution (prepared by bubbling the gas through water) is what is generally called hydrochloric acid or muriatic acid.

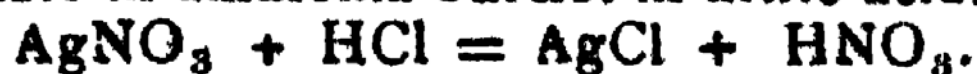
When a concentrated aqueous solution of the acid is heated it becomes more and more dilute until a mixture containing nearly 20 p.c. of the real acid distils unchanged at 110°C . If, on the other hand, we distil a dilute solution, it gradually loses water until the concentration reaches 20 p. c. at the 'constant boiling-point' 110°C .

Chemical.—Hydrogen chloride does not burn, nor does it support combustion. In the gaseous or liquefied condition it is not so active as in aqueous solution.

The aqueous solution of hydrogen chloride is strongly acid in its properties; it dissolves many metals, forming chlorides and liberating hydrogen. [See below, Chlorides].

Tests.—(1) Hydrochloric acid *gas* forms with ammonia dense white fumes of ammonium chloride (NH_4Cl).

(2) *Aqueous* hydrochloric acid (*a*) when heated with manganese dioxide produces chlorine, and (*b*) when added to silver nitrate produces a white curdy precipitate of silver chloride which is soluble in ammonia but not in nitric acid.



Composition.—The composition of hydrochloric acid may be proved both analytically and synthetically by a number of experiments amongst which the following are the chief :

- **Analytic Methods :** (1) **Electrolysis.**—By electrolysis of hydrochloric acid we find it to consist of equal volumes of hydrogen and chlorine. The experiment is performed in Hofmann's apparatus which consists of three glass tubes connected at the bottom : two of the tubes have stopcocks at the top and carbon electrodes at the lower ends; the bulb tube serves as the reservoir for the solution of hydrochloric acid.

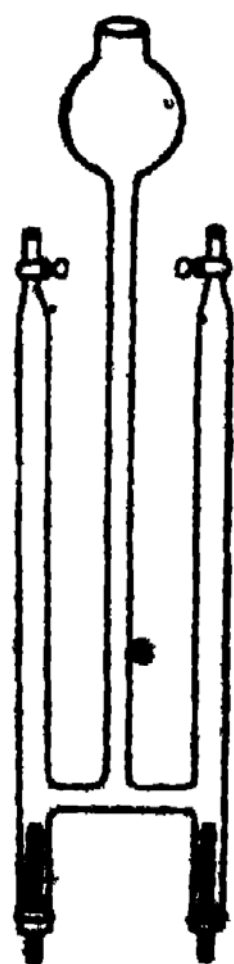


Fig. 41. On filling the apparatus with strong solution of hydrochloric acid and then passing an electric current, hydrogen is evolved, and chlorine which is also liberated is dissolved by the liquid. After some time (when the liquid has become saturated with chlorine), *hydrogen and chlorine are evolved in equal volumes*—the former from the negative and the latter from the positive electrode. [$2\text{HCl} = \text{H}_2 + \text{Cl}_2$].

(2) **Action on Sodium Amalgam.**—If we pass sodium amalgam (*i.e.*, a solution of sodium in mercury) into a tube which con-

tains hydrochloric acid gas and stands over mercury, the sodium combines with chlorine, and the residual gas which is found to be hydrogen occupies only half the volume of the original gas (both volumes being measured at the same temperature and pressure). This shows that *hydrochloric acid gas contains half its volume of hydrogen*.



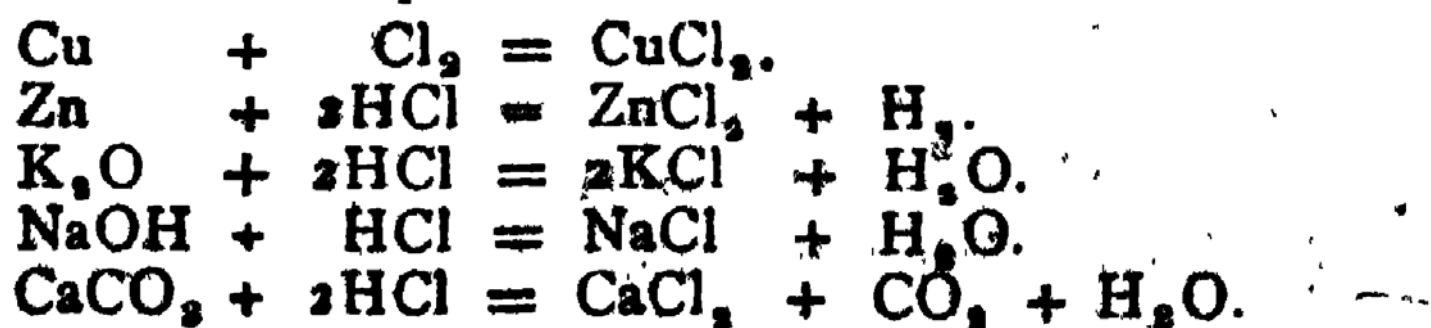
Synthetic Method.—A stout glass tube having stopcocks at both ends is filled with a mixture of hydrogen and chlorine in equal volumes, and the gases made to combine by exposing the tube to strong daylight or an electric spark. On opening a stopcock of the cool tube under mercury, no mercury rises in the tube, nor does any excess of gas escape. But on opening the stopcock under water, the resultant hydrochloric acid dissolves in water which fills the tube completely. This shows that *1 volume of hydrogen and 1 volume of chlorine combine to form 2 volumes of hydrochloric acid gas*.



The Formula HCl.—Since 2 volumes of hydrochloric acid gas contain 1 volume of hydrogen and 1 volume of chlorine, and as the densities of the gases are 18.25, 1, and 35.5 respectively, it follows that 36.5 parts of hydrochloric acid contain 1 part of hydrogen and 35.5 parts of chlorine. These numbers correspond to the formula HCl for hydrochloric acid.

Uses.—Hydrochloric acid is employed for the manufacture of chlorine, sal-ammoniac, tin chloride, &c.

Chlorides.—Chlorides are the compounds of chlorine with elements other than oxygen. The salts of hydrochloric acid, *i. e.*, chlorides of metals, occur plentifully in nature. They are formed by the direct union of chlorine with a metal, or by the action of hydrochloric acid on a metal, or its oxide, hydroxide, or carbonate. For example—



Most metallic chlorides evolve hydrochloric acid when heated with sulphuric acid, and give off chlorine when heated with a peroxide. All soluble chlorides, when added to a solution of silver nitrate, produce a *white* curdy precipitate of silver chloride (which is soluble in ammonia).

OXIDES AND OXYACIDS OF CHLORINE.

[Chlorine unites with hydrogen to form HCl , and with nitrogen to form chloride of nitrogen (NCl_3). It does not directly combine with oxygen, but is made to do so indirectly].

The following oxides and oxyacids of chlorine are known; they form two series which illustrate the law of Multiple Proportions:

Cl_2O	Chlorine monoxide or Hypochlorous anhydride.	HClO	Hypochlorous acid.
ClO_2	Chlorine peroxide.	HClO_2	Chlorous acid (?)
Cl_2O_7	Perchloric anhydride.	HClO_3	Chloric acid.
		HClO_4	Perchloric acid.

These compounds are more or less unstable bodies, and so cannot be preserved. Chlorous acid (HClO_2) has not been made; but its salts (called *chlorites*) are familiar.

CHLORINE MONOXIDE (Cl_2O) and HYPOCHLOROUS ACID (HClO).

Chlorine monoxide is prepared by passing dry chlorine over dry precipitated mercuric oxide—



It is a pale yellow gas with chlorine-like smell. When heated, it decomposes with explosion. It dissolves in water forming hypochlorous acid—

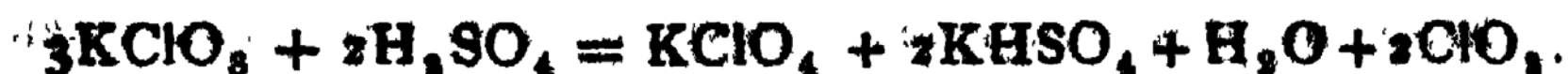


Hypochlorous acid has a yellowish colour and chlorous smell. It is very unstable, but is a powerful bleaching agent.

Of the salts of this acid, called *hypochlorites*, bleaching powder (chloride of lime) is the most important.

CHLORINE PEROXIDE (ClO_2).

This gas is prepared by gently heating potassium chlorate with strong sulphuric acid—



It is a deep yellow gas with chlorous smell. The slightest heat or light decomposes it with violent explosion. It is a powerful oxidizing agent: phosphorus burns in it spontaneously.

CHLORIC ACID (HClO_3).

It is prepared by the action of sulphuric acid on an aqueous solution of barium chlorate—



It has powerful oxidizing properties: wood, paper, &c. are instantly charred and burnt by it.

Its salts, called *chlorates*, of which potassium chlorate is the chief, are more stable than the acid. They are soluble in water and yield oxygen when heated.

PERCHLORIC ACID (HClO_4).

This acid is prepared by the action of strong sulphuric acid on dry potassium perchlorate—



It is a clear fuming liquid, and is a very strong oxidizing agent. It is highly explosive and decomposes even in the dark. It produces a hissing sound when dropped into water, for which it has great affinity.

The salts of this acid, called *perchlorates*, are soluble in water, and evolve oxygen when heated.

University Examination Questions.

1. What are the leading members of the chlorine family? Mention all the properties you know of that are common to the group. What relation is found to hold between their atomic weights and the other properties found in a different degree in each? [A. 93.]

Chlorine, bromine, and iodine are said to be members of a family of elements. Compare the properties of these elements and of their compounds that you have studied, and hence prove the correctness of the above statement [C. 1911; A. 1913.]

Compare chlorine, bromine and iodine, stating the points of

resemblance and difference [A. 96]. Name the halogens ; write down carefully the properties of each [A. 03].

2. Mention the formulæ of the various oxyacids of each of the Halogens [A. 07].

I

1. How would you prepare chlorine ? Sketch the apparatus you would use and write the equation representing the chemical action taking place [C. 94, 98, 07, 1916 ; A. 95, 1900, 04, 07.]

How many grammes of chlorine would you prepare from 100 grammes of sal-ammoniac ? [A. 95].

2. Give the important physical and chemical properties of chlorine [C. 94, 07, 1900, 13, 16 ; A. 95, 1900, 04, 07]. Explain its action as a bleaching agent [A. 04]. What are its uses ? [A. 07].

What chemical changes occur when chlorine is passed (a) into cold dilute caustic potash, (b) into hot caustic potash, (c) over phosphorus, (d) into slaked lime ? [A. 05]. What would happen if you pass chlorine gas through (a) solution of ammonia, (b) slaked lime, (c) sulphuretted hydrogen ? [C. 1916].

3. Mention the chief compounds of chlorine with hydrogen and oxygen, giving their various chemical formulæ [C. 94 ; A. 94].

4. Describe carefully, making a sketch of the apparatus, how you would prepare and collect hydrochloric acid gas [C. 96, 01, 1911, 15 ; A. 1900]. State its principal properties [C. 96] and uses [C. 1911].

What quantity of common salt would be required for the production of 50 grams of hydrochloric acid ? [C. 96].

120 grams of common salt are decomposed by sulphuric acid. What is the volume of Hydrochloric Acid gas produced at 15° C. and 740 mm. pressure,— if NaHSO_4 is the residue left in the retort ? [A. 07].

5. What is the action of hydrochloric acid on (a) zinc, carbon, manganese dioxide, calcium carbonate, caustic soda [C. 99] ; (b) copper oxide, manganese dioxide, caustic soda ? [A. 08].

How can chlorine be distinguished from hydrochloric acid gas ? [C. 98]. How would you distinguish hydrochloric acid gas from SO_2 . [C. 96, 01].

What experiments would you make to show the difference in properties between a *mixture* of equal volumes of hydrogen and

chlorine and the *compound* formed by the chemical union of these two gases? [C. 1912].

6. How would you determine the composition of hydrochloric acid gas? [C. 03, 05; A. 02, 08]. Describe the means by which you would ascertain its formula [A. 1900, 01].

7. Write down the chemical formulæ for hydrochloric, [sulphurous, sulphuric] chlorous and chloric acids. What names are given to the salts produced when a base is acted on by the above acids? Give examples. [A. 93].

SECTION II.

Bromine and its Compounds.

BROMINE.

ATOMIC WEIGHT 80. VAPOUR DENSITY 80.

MOLECULAR FORMULA Br_2 .

Occurrence.—Bromine is found in combination (with potassium, sodium, and magnesium) in sea-water, mineral waters, and salt deposits.

Preparation.—(1) In the laboratory, bromine is prepared by heating in a retort a mixture of potassium bromide, manganese dioxide, and sulphuric acid. (Compare the preparation of chlorine). The apparatus used for the preparation of nitric acid is employed in this case, and liquid bromine distils over. The reaction is expressed in two ways—



(2) Bromine may also be prepared by passing chlorine through a solution of potassium or magnesium bromide : *



Manufacture.—Bromine is manufactured chiefly from crude *carnallite* ($\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$) obtained at Stassfurt (in Germany). This salt contains small quantities of magnesium bromide. Potassium chloride is first separated; the hot mother-liquor (called *bittern*) is then made to trickle down over round stones in a tower, where it meets an ascending stream of chlorine. Bromine is thus liberated (see the last equation above), and its vapour is condensed in a worm.

Properties: Physical.—Bromine is a heavy reddish-brown liquid. [It is the only non-metallic element that is liquid at ordinary temperatures]. It is poisonous and has a more irritating smell than that of chlorine: hence the name 'bromine,' signifying stench. It is volatile and gives off brown vapours. It dissolves in water forming a red solution called *bromine water*.

Chemical.—Bromine resembles, but is less active than, chlorine. It is non-inflammable and a non-supporter of combustion. But a jet of burning hydrogen continues to burn in bromine vapour (forming hydrogen bromide), and phosphorus unites with it as with chlorine. Bromine has got moderate bleaching properties.

Tests.—(1) Bromine is recognised by its colour and odour.
 (2) It produces a yellow colour in contact with starch.
 (3) When bromine-water is shaken with a little ether or carbon disulphide, bromine is dissolved and a brown layer is formed in the water.

Uses.—Bromine is chiefly used in the manufacture of aniline dyes and in the preparation of potassium bromide which is employed in medicine and in photography.

HYDROBROMIC ACID OR HYDROGEN BROMIDE.

FORMULA HBr . MOLECULAR WEIGHT 81. DENSITY 4.05.

Preparation.—(1) This acid is prepared by adding bromine to a mixture of red (amorphous) phosphorus and water. Red phosphorus and water are placed in a flask which is furnished with a dropping funnel and a delivery tube leading through a U-tube containing also phosphorus. On bromine being allowed to drop from the stoppered funnel into the flask, hydrobromic acid is evolved. The gas is freed from bromine vapour in

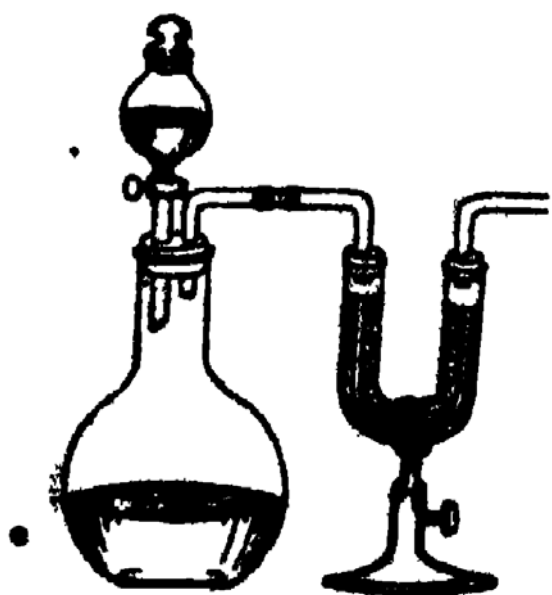
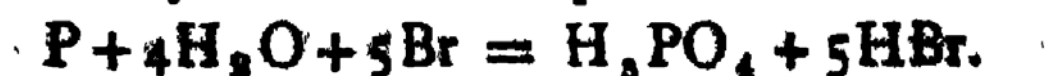
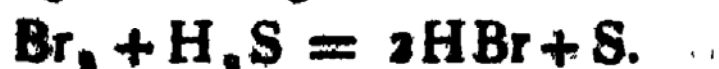


Fig. 42.

its passage through the phosphorus contained in the U-tube and is collected by downward displacement.



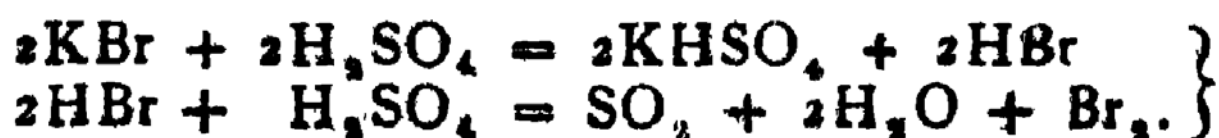
(2) In aqueous solution the acid is formed by passing sulphuretted hydrogen through bromine-water :



Properties.—Hydrogen bromide resembles hydrogen chloride in its properties. It is a colourless fuming gas with a pungent smell. It dissolves in water to form the aqueous acid and is decomposed by chlorine with the liberation of bromine :



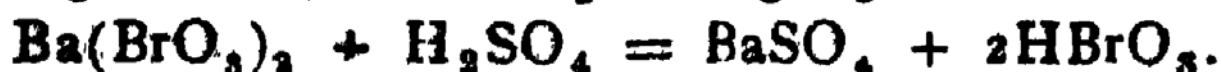
Bromides —The salts of hydrobromic acid, *i. e.*, metallic *bromides*, are similarly decomposed by chlorine. When heated with sulphuric acid they produce a mixture of hydrobromic acid and free bromine :



On the addition of silver nitrate ($AgNO_3$) to a solution of a bromide, a *yellowish white* precipitate of silver bromide is formed, which is only sparingly soluble in ammonia.

OXYACIDS OF BROMINE.

No oxides of bromine are known. There are two oxyacids, *viz.*, hydrobromous acid ($HBrO$) and bromic acid ($HBrO_3$). These acids resemble respectively hydrochlorous acid and chloric acid in their properties. They are also prepared by the same methods, bromine and barium bromate being respectively used instead of chlorine and barium chlorate—



Salts of bromic acid, called *bromates*, resemble chlorates.

University Examination Questions (*contd.*).

II

1. How may bromine be prepared? What are its physical and chemical properties? [A. 09].

Describe the commercial sources and preparation of bromine. How is it chemically purified, and what are its uses? [A. 1915].

2. Write down carefully all the properties of bromine and describe the preparation of hydrobromic acid. Sketch the apparatus you would use [A. 01].

3. How does chlorine differ from bromine in chemical and physical properties? What is the action of each on dilute and cold solution of caustic soda and on solution of potassium iodide? Give equations. [C. 02].

SECTION III.

Iodine and its Compounds.

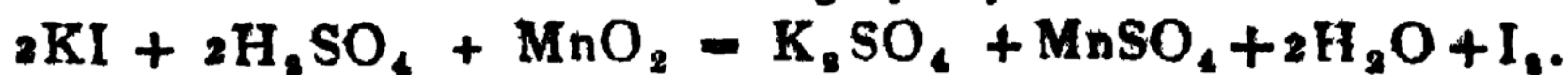
IODINE.

ATOMIC WEIGHT 127. VAPOUR DENSITY 127.

MOLECULAR FORMULA I_2 .

Occurrence.—Iodine is found in combination with sodium, potassium, &c. in sea-weeds and in crude Chili saltpetre (called *caliche*).

Preparation.—(1) It is prepared by heating in a retort potassium iodide or sodium iodide with manganese dioxide and sulphuric acid. Violet vapours of iodine are given off: these distil over and condense as dark grey crystals.



[Compare the preparation of chlorine and of bromine].

(2) Iodine is also liberated when either chlorine or bromine is passed through potassium iodide:



Manufacture: (i) From Sea-weeds.—The following are briefly the steps involved: (1) Sea-weeds are dried and burnt, whereby an ash named *kelp* is obtained; (2) the kelp is lixivated with water, which separates all soluble salts from the charcoal, and on evaporation throws down the less soluble salts; (3) sulphuric acid is next added to the concentrated liquid, whereby sulphur is precipitated from sulphides, &c.; (4) on

heating the mother-liquor (which now contains iodides, bromides, &c.) with manganese dioxide, iodine vaporizes and is condensed in special earthenware jars called *aludels*.

(ii) From Caliche.—Iodine is present in *caliche* as sodium iodate. After removal of sodium nitrate from *caliche*, the mother-liquor is treated with sodium bisulphite, whereby iodine is precipitated as a black solid which is then sublimed.

Properties: Physical.—Iodine is a greyish black crystalline solid. When heated it easily melts and boils, yielding violet vapours (whence the name 'iodine') which smell like dilute chlorine. Iodine is poisonous and stains the skin. It dissolves slightly in water, but readily in an aqueous solution of potassium iodide and in ether, alcohol, &c.

Chemical.—Iodine is less active than chlorine and bromine, either of which displaces iodine from an iodide (see above). It has very feeble bleaching properties. It does not burn and does not support combustion; but it unites with many metals forming iodides, and readily ignites phosphorus. It forms a blue compound with starch.

Test.—A solution of starch is turned blue by *free* iodine. [When a solution of potassium iodide alone is added to starch paste, there is no change of colour. But with the addition of a little chlorine-water or bromine-water, a blue colour is at once produced, owing to the liberation of free iodine].

Uses.—Iodine is principally used in medicine, and in the preparation of dyeing colours. Potassium iodide is employed in photography.

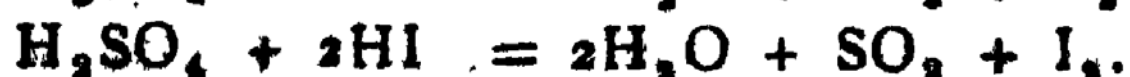
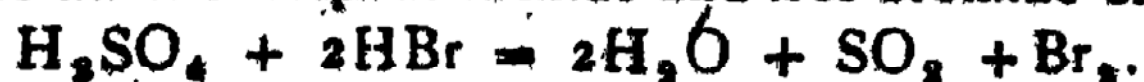
HYDRIODIC ACID OR HYDROGEN IODIDE.

FORMULA HI. MOLECULAR WEIGHT 128. DENSITY 6.4.

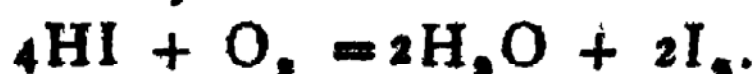
Preparation.—This acid is prepared in the same way as hydrobromic acid, iodine being substituted for bromine. The reactions are exactly similar.

NOTE.—Hydrochloric acid is easily prepared by the action of H_2SO_4 upon a chloride. But as the affinity of hydrogen for bromine or iodine is less than its affinity for chlorine, hydrobromic and

hydriodic acids cannot be prepared by the action of H_2SO_4 upon a bromide and an iodide respectively. Thus, when H_2SO_4 is added to potassium bromide or iodide, hydrobromic or hydriodic acid is at first formed; but part of it immediately reduces H_2SO_4 with the liberation of sulphur dioxide and free bromine or iodine.



Properties.—Hydriodic acid resembles HCl and HBr in its properties. But it is very unstable: even an aqueous solution of it decomposes by contact with air.



Iodides.—Hydriodic acid and its salts (iodides) liberate iodine on the addition of chlorine or bromine. When silver nitrate is added to their solutions, a *yellow* precipitate of silver iodide is formed which is insoluble in ammonia.

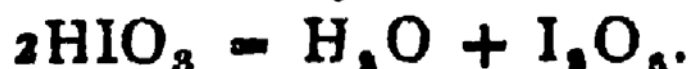
OXIDE AND OXYACIDS OF IODINE.

- IODIC ACID (HIO_3) , IODINE PENTOXIDE OR IODIC ANHYDRIDE (I_2O_5) .

Iodic acid is prepared (1) by heating iodine with strong nitric acid, or (2) by treating a solution of barium iodate with sulphuric acid.



Iodic acid yields iodic anhydride when heated—



Both these compounds are white solids, soluble in water and stable bodies. The salts of iodic acid are called *iodates*.

PERIODIC ACID.

The true formula of this acid is HIO_4 ; but as it can only be obtained diluted with water, it is expressed by the formula $(\text{HIO}_4, 2\text{H}_2\text{O})$ or H_5IO_6 . It is obtained by adding iodine to an aqueous solution of perchloric acid—



• It is a colourless, deliquescent, crystalline body. Its salts are called *periodates*.

University Examination Questions (*contd.*)

III.

1. Point out the analogy and difference between Chlorine and Iodine. Tabulate their derivatives, both acids and salts, naming them and giving appropriate formulæ [C. 05].

2. How is Iodine prepared? What are its properties? [C. 09; A. 96]. How is iodine obtained from kelp? Describe its important physical and chemical properties. [C. 14].

How is Iodine prepared from Seaweed? What weight of Iodine is liberated from excess of potassium iodide by the action of one litre of chlorine measured at 10° C. and 750 m.m. pressure? [A.08].

How is iodine obtained (a) from kelp, and (b) from caliche? [A. 1911].

3. How would you prepare hydriodic acid; make a sketch of the apparatus you would use [C/ 1915; A. 03, 06, 1910, 1912]. Give a detailed account of experiments you would perform in illustration of the properties of the compound [A. 1910].

Hydrochloric acid is prepared by the action of sulphuric acid upon sodium chloride. What happens if an iodide or a bromide is substituted for the chloride? [A. 06]. Can you prepare hydriodic acid in the same way in which hydrochloric acid is ordinarily prepared? If not, why not? [C. 14].

State how you would distinguish between a 'chloride' and an 'iodide'. [C. 1915.]

4. Describe carefully how you would prepare and test iodic acid [A. 1912].

CHAPTER XXIV.

SULPHUR AND ITS COMPOUNDS.

SECTION I.

SULPHUR.

SYMBOL S. ATOMIC WEIGHT 32. MOLECULAR WEIGHT 64.

Occurrence.—Sulphur, also called *brimstone* (= 'burning stone'), is found in its native state in the vicinity of volcanoes. In combination with metals, it is found in large quantities as

the sulphides—*iron pyrites* (FeS_2), *copper pyrites* (Cu_2FeS_4), *galena* (PbS), *zinc blende* (ZnS), *cinnabar* (HgS), &c. Combined with metals and oxygen, sulphur occurs as the sulphates—*gypsum* ($\text{CaSO}_4, 2\text{H}_2\text{O}$), *heavy spar* (BaSO_4), *Glauber's salt* ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$), *Epsom salt* ($\text{MgSO}_4, 7\text{H}_2\text{O}$), &c. Sulphur is also present in small quantities in many organic compounds, such as the white of egg.

Preparation.—I. The preparation of sulphur from native sulphur or from its ore (iron pyrites) consists of two stages, *vis.*, Extraction and Purification:

(i) Native sulphur is a rocky substance containing earthy impurities. To separate sulphur from these impurities, the sulphur rock is piled up on a sloping floor and then ignited. A part of the sulphur burns, and the heat produced thereby melts the rest which is drawn off into moulds. Crude sulphur is obtained from iron pyrites by a similar process.

(ii) Crude sulphur obtained by extraction is next refined by distillation. The sulphur is first melted in an iron-pot (P in Fig. 43) whence it is passed into an iron-retort (R) where it is boiled by means of the fire (F). The vapour of sulphur on reaching the brick-built chamber (C) at once solidifies, and falls to the bottom as a fine powder called 'flowers of

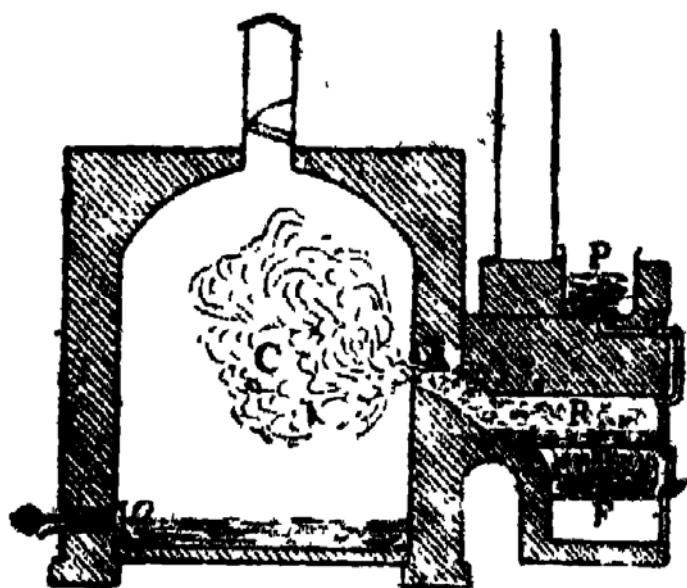


Fig. 43.

—sulphur.' But afterwards when the chamber becomes hot, the vapour condenses into the liquid state; this liquid is then drawn off through the opening (o) and cast into cylindrical moulds where the sulphur solidifies. This is the familiar 'roll sulphur' or 'stick sulphur.'

II. Sulphur is now also recovered from the *soda-waste* obtained in Leblanc's method of alkali manufacture. The waste (containing calcium sulphide) is treated with carbon dioxide in presence of water: the sulphuretted hydrogen evolved

is then mixed with air and decomposed by ferric hydroxide, whereby sulphur is deposited.

Effect of Heat on Sulphur.—The effect of heat on sulphur is to produce a series of changes which become more remarkable when at different temperatures molten sulphur is allowed to cool.

(i) Sulphur when gently warmed melts (at $114^{\circ}\text{C}.$) to a clear pale yellow liquid. [This liquid when cooled forms the *prismatic* variety of sulphur].

(ii) When further heated the liquid darkens and thickens until (at about $200^{\circ}\text{C}.$) it is almost black and perfectly *viscid*.

(iii) With increase of temperature (up to 400°) the sulphur again becomes mobile. [At this liquid stage *plastic sulphur* is prepared].

(iv) Finally, at about $448^{\circ}\text{C}.$, the liquid boils forming brown vapours. [These vapours condense to form *flowers of sulphur*].

Allotropic Forms of Sulphur.—There are principally four allotropic modifications of sulphur, *viz.*, (1) Rhombic or Octahedral, (2) Prismatic or Monoclinic, (3) Plastic, and (4) White Amorphous. The first two forms are *crystalline*, while the last two are *amorphous*.

(1) Rhombic Sulphur.—This is the form in which native sulphur occurs, and is the most ordinary and stable form of sulphur. Its specific gravity is 2.05. It is soluble in carbon disulphide, and is therefore artificially obtained by evaporating a solution of roll sulphur in carbon disulphide. *Flowers of sulphur* belong to this class.

(2) Prismatic Sulphur.—This variety is prepared in the following way:—Sulphur is melted in a crucible, and then allowed to cool until a crust forms on the surface. The crust is broken through and the liquid sulphur poured out: yellow needle-like crystals are found to have formed round the side of the crucible. Prismatic sulphur is transparent and brittle; but it is unstable and changes into the rhombic variety after some time. Its specific gravity is 1.98, and it is soluble in carbon disulphide.

(3) **Plastic Sulphur.**—When thick and dark molten sulphur (which is near the boiling point) is poured into water, a soft, elastic, yellow, transparent substance is produced: this is called 'plastic sulphur.' It is soon changed into ordinary brittle sulphur. Its specific gravity is 1.95, and it is insoluble in carbon disulphide.

(4) **White Amorphous Sulphur.**—It occurs, in small quantities, mixed with 'flowers of sulphur,' from which it can be separated by means of carbon disulphide. It is also obtained as a finely-divided yellowish white powder (called *milk of sulphur*) by boiling flowers of sulphur and slaked lime in water and then precipitating the filtrate with hydrochloric acid, washing and drying. White powder-sulphur is insoluble in carbon disulphide and passes into the ordinary yellow form when heated.

Properties : Physical.—Sulphur is a brittle yellow solid. It undergoes a series of changes when heated (see above). It exists in four important allotropic forms which differ to a certain extent in their properties (see above). As sulphur has two distinct crystalline forms (one being produced from solution, the other from fusion), it is called *dimorphous*. Sulphur is a very bad conductor of heat and electricity.

Chemical.—Sulphur burns in the air with a pale blue flame, forming sulphur dioxide [$S + O_2 = SO_2$]. It combines with many metals to form *sulphides*, and supports combustion in some cases. Thus, when copper-foil is introduced into the vapour of boiling sulphur, it burns brilliantly with the formation of copper sulphide.

Tests.—(1) Sulphur burns with its peculiar blue flame and suffocating odour. (2) Sulphur (whether in the free or combined state) when heated with strong nitric acid yields sulphuric acid.

Uses.—Sulphur is used in the manufacture of matches, gun-powder, sulphuric acid, &c.

University Examination Questions.

1. Name the principal compounds of sulphur found in the crust of the earth, and describe the method you would use to prove that any one of them contains sulphur [C. 05.]

2. How is roll sulphur commercially obtained? [C. 14].
3. Describe the allotropic forms of sulphur. How are they obtained? [C. 1911, 14; A. 08]. Compare the properties of the allotropic forms of sulphur. [C. 02].

SECTION II.

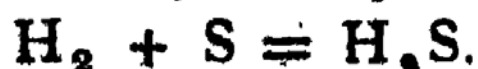
SULPHURETTED HYDROGEN.

(*Hydrogen Sulphide or Hydrosulphuric Acid*).

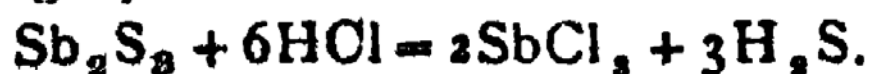
FORMULA H_2S . MOLECULAR WEIGHT 34. DENSITY 17.

Occurrence.—It is found in volcanic regions and in mineral 'sulphur waters.' It is also formed by the putrefaction of animal matters containing sulphur (such as eggs), and by the destructive distillation of coal.

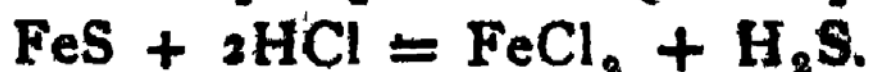
Preparation —(1) The gas may be synthetically prepared by passing hydrogen over boiling sulphur, or by passing a mixture of hydrogen and sulphur vapour through a hot tube:



(2) The pure gas is obtained by heating antimony trisulphide with strong hydrochloric acid:



(3) *The gas is generally prepared by the action of dilute sulphuric or hydrochloric acid upon ferrous sulphide.* Fragments of ferrous sulphide are placed in a flask and the dilute acid is poured through a thistle funnel: the gas is readily evolved without the application of heat, and is collected by displacement of *warm* water (Fig. 13), or by downward displacement.



Kipp's Apparatus.—As sulphuretted hydrogen is constantly required in the laboratory for analytical purposes, it is readily prepared in what is known as Kipp's apparatus (Fig. 44). The apparatus has two parts: the lower part consists of two glass globes (*a, b*) joined by a neck; and the upper part consists of a glass globe having a long stem which passes air-tight through the neck of the middle globe and reaches the lower-

most one. The middle globe has an outlet (*d*) where the delivery tube (provided with a stopcock) is fitted in. The uppermost globe is furnished with a funnel-tube.



Fig. 44.

Ferrous sulphide is inserted into the middle globe through the outlet, and (the stopcock *e* being open) sulphuric acid is poured through the funnel until the acid fills the globe (*a*) and reaches the ferrous sulphide in globe (*b*). The evolution of the gas soon commences. When the gas is no longer required, the tap (*e*) is closed, and the pressure of the gas produced forces the acid in globe (*a*) up through the stem, so that the acid cannot

come in contact with ferrous sulphide. Further evolution of the gas is thereby stopped, until the tap is opened again.

This apparatus is also used to obtain a ready supply of hydrogen, zinc being substituted for ferrous sulphide.

Properties: Physical.—Sulphuretted hydrogen is a colourless gas having the offensive *smell of rotten eggs*. It *dissolves in cold water*, and imparts its own smell to the solution. When inhaled in the pure state it is poisonous. It is heavier than air, and can be changed rather easily into the liquid and solid states.

Chemical.—1. *It burns with a bluish flame.* When the supply of air or oxygen is limited (as when the gas burns in a jar), sulphur is deposited on the inside of the vessel:



But when there is free access of air, water and sulphur dioxide are produced:



A mixture of two volumes of H_2S and three volumes of oxygen explodes violently when ignited.

2. *An aqueous solution of the gas has feeble acid properties.* Hence it is sometimes called 'hydrosulphuric acid' or 'sulphydric acid.' Sulphuretted hydrogen acts upon many metals and metallic salts to form *sulphides*. Thus silver, lead, &c. are tarnished in contact with the gas, owing to the formation of the sulphides. (See below).

Solution of soda or of lime absorbs sulphuretted hydrogen forming a 'hydrosulphide.'



3. *Sulphuretted hydrogen is a reducing agent*, and when it is acted upon by (a) oxygen, (b) the halogens, (c) sulphur dioxide, (d) sulphuric acid, and (e) a ferric salt, sulphur is deposited in each case :

(a) Oxygen of the air has no action on dry sulphuretted hydrogen, but slowly decomposes its aqueous solution—



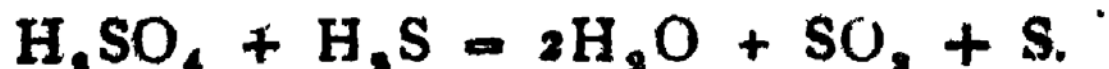
(b) When sulphuretted hydrogen is brought in contact with the halogens, reactions of the following nature take place—



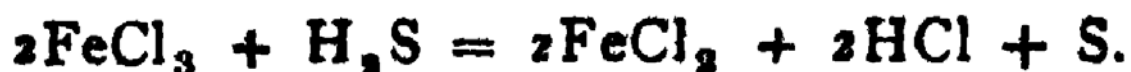
(c) Sulphuretted hydrogen reduces sulphur dioxide : as both these gases are evolved from volcanoes, native sulphur is probably also formed by this reaction—



(d) The following reaction explains why sulphuretted hydrogen cannot be dried by being passed through sulphuric acid—



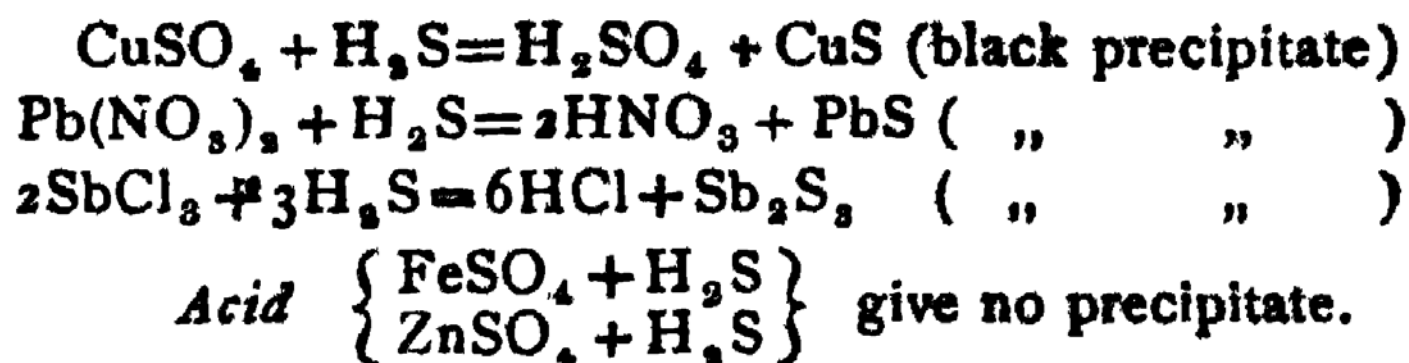
(e) When sulphuretted hydrogen is passed through a solution of ferric chloride, the salt is reduced to the ferrous state—



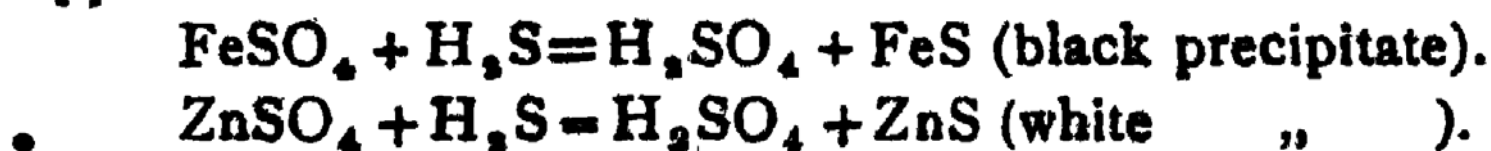
Sulphides : Sulphuretted Hydrogen as a Reagent.—Sulphides are the compounds of metals with sulphur, such are ferric sulphide (iron pyrites, FeS_2), lead sulphide (galena,

PbS), silver sulphide (Ag_2S), &c. Most sulphides are insoluble in water (those of sodium, calcium, magnesium, &c., being exceptions). The sulphides of the metals antimony, arsenic, bismuth, cadmium, copper, lead, mercury, and tin, are insoluble in *dilute acids*; while the sulphides of aluminium, chromium, cobalt, iron, manganese, nickel, and zinc, are insoluble in *alkaline liquids*. Sulphides of different metals have also characteristic colours. These two peculiarities (solubility and colour) enable us to detect a sulphide of a particular metal.

When sulphuretted hydrogen is passed through the solution of some metallic salts, sulphides of the particular metals are precipitated. Hence, sulphuretted hydrogen is a valuable reagent in chemical analysis (see Appendix). By its means we can (1) identify many metals in their solutions, and (2) separate them from one another in a mixture. Thus, if we pass sulphuretted hydrogen through the *acidulated* solutions of the following salts—copper sulphate, lead nitrate, antimony chloride, ferrous sulphate, and zinc sulphate—the results will be as follows:



Sulphides of copper, lead, and antimony being insoluble in the acid are precipitated. But as the sulphides of iron and zinc are soluble in the acid, no precipitate is formed by the passage of sulphuretted hydrogen through their acid solutions. If however a little ammonia or any other *alkali* be added to the solutions (so as to neutralize the acid), precipitates at once appear:



Tests.—(1) Sulphuretted hydrogen is known by its odour.
(2) A piece of paper moistened with a solution of lead

acetate is stained black by sulphuretted hydrogen (owing to the formation of black lead sulphide).

Composition.—If tin is heated in a known volume of sulphuretted hydrogen, tin sulphide is formed and the volume of the liberated hydrogen is found to be equal to the volume of sulphuretted hydrogen used. Hence, *hydrogen sulphide contains its own volume of hydrogen.*

As 2 volumes of sulphuretted hydrogen contains 2 volumes of hydrogen and as the densities of the gases are 17 and 1 respectively, 34 parts of sulphuretted hydrogen must contain 2 parts of hydrogen and 32 parts of sulphur. Hence, the formula of sulphuretted hydrogen is H_2S .

University Examination Questions.

1. State what you know of the occurrence of Sulphuretted Hydrogen in nature [A. 98].

2. Describe the preparation of sulphuretted hydrogen [C. 95, 97, 1910, 15; A. 95, 98, 07, 13]. Sketch the apparatus used in its preparation [C. 04, 1910; A. 1913].

Make a careful diagrammatic drawing of Kipp's apparatus and explain how it is used for the preparation of sulphuretted hydrogen gas [C. 09, 13].

3. Describe the properties of sulphuretted hydrogen [C. 95, A. 98]. State the physical properties of the compound. Is it an acid, or a base, or a neutral substance? How would you prove your statement? [C. 10]. What happens when the gas is burnt? [C. 97].

Compare the physical and chemical properties of the hydrogen compounds of nitrogen and sulphur [C. 1915].

4. Explain fully the use of sulphuretted hydrogen as a chemical reagent [C. 95, 97, 09, 1911; A. 95, 07]. How and why is this reagent used in the separation of lead, zinc, and calcium from a mixture of solutions of the nitrates of these metals? [C. 1900].

5. Describe what takes place when sulphuretted hydrogen is passed through solutions of (a) caustic potash, (b) lead nitrate, (c) arsenic trioxide [A. 95]; (d) lead nitrate, (e) antimony chloride (f) sodium hydrate [C. 02], (g) silver nitrate, (h) copper sulphate [C. 04]; (i) copper sulphate, (j) ferrous chloride, (k) magnesium sulphate [C. 1915].

6. What volume of sulphuretted hydrogen at 20°C. and 720 m.m. is required to convert 1 gram of copper sulphate ($\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$) into copper sulphide? How much ferrous sulphide would be required to yield the requisite volume of sulphuretted hydrogen? [A. 1910].

7. What volume of sulphur dioxide would you get at 15°C. and 740 m.m. by burning sulphuretted hydrogen obtained from 11 grammes of sulphide of iron? $\text{Fe} = 56$. $\text{S} = 32$. [C. 1913].

8. By what tests would you recognise sulphuretted hydrogen? [C. 1900, 09; A. 1900].

9. How would you determine the composition of the gas? [C. 1900, 09; A. 1913].

SECTION III.

Oxides and Oxyacids of Sulphur.

SULPHUR DIOXIDE OR SULPHUROUS ANHYDRIDE.

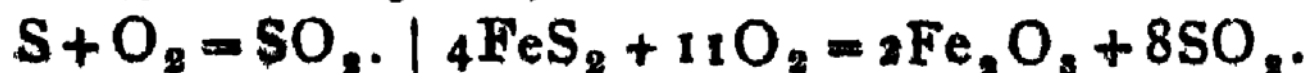
FORMULA SO_2 . MOLECULAR WEIGHT 64. DENSITY 32.

Occurrence.—This gas is given off from volcanoes, and is sometimes found in the air of large towns.

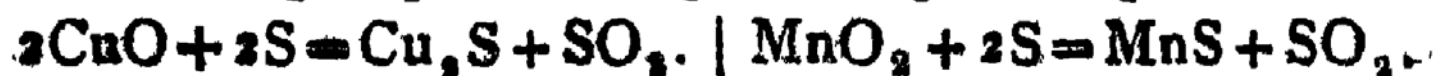
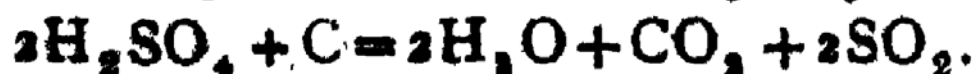
Preparation.—(1) In the laboratory the gas is prepared *by heating strong sulphuric acid with copper*. [Mercury, lead, or silver may be used instead of copper]. The evolved gas may be dried by bubbling it through strong sulphuric acid, and is then collected by downward displacement (or over mercury). See Fig. 15.



(2) On the large scale it is obtained *by burning sulphur or iron pyrites (ferric sulphide) in air*.



(3) & (4) It may also be prepared *by heating strong sulphuric acid with sulphur or carbon*, as also *by heating sulphur with copper oxide or manganese dioxide*.



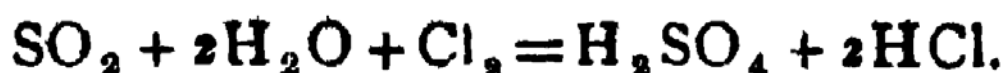
Properties : Physical.—Sulphur dioxide is a colourless gas having a pungent suffocating smell. Of all the gases it is the most easily condensible: liquid sulphur dioxide is obtained by passing the dry gas through a spiral tube immersed in a freezing mixture (*i. e.* a mixture of ice and salt).

Chemical.—1. *It does not burn, nor does it ordinarily support combustion.* But finely-divided iron and some other metals burn when heated in the gas, and lead peroxide (PbO_2) glows in it spontaneously with the formation of lead sulphate (PbSO_4).

2. *It unites with water, forming sulphurous acid (H_2SO_3).*

3. *It is a powerful reducing and bleaching agent.* Thus, when moist red roses are placed in a jar of the gas, the colour of the flowers is at once destroyed. Its action on potassium bichromate and iodic acid are further examples of reduction. (See below).

4. In presence of water it converts chlorine into hydrochloric acid: hence its use as an antichlor.



5. Sulphur dioxide and sulphuretted hydrogen decompose each other with the liberation of sulphur:



Comparison of Chlorine and Sulphur Dioxide as bleaching agents.—Chlorine and sulphur dioxide agree in this respect that both bleach in presence of water. Their modes of action are however reverse to each other:

(1) *Chlorine bleaches by oxidation.* It liberates oxygen from water [$\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$], and the nascent oxygen oxidizes the colouring matters with the production of colourless compounds. On the other hand, *sulphur dioxide bleaches by reduction.* In this case hydrogen is liberated [$\text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{H}$], and the nascent hydrogen reduces the colouring matters to colourless compounds.

(2) *Decolorization by chlorine is permanent, i. e., once a substance is bleached by chlorine the original colour cannot*

be restored. Whereas, *decolorisation by sulphur dioxide is restorable* : in this case the original colour can be reproduced when the bleached substances are treated with dilute sulphuric acid or with a weak alkali. Hence, bleached flannel gradually becomes yellowish when washed with soap.

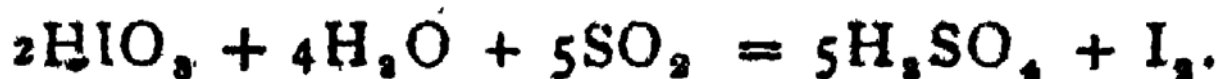
(3) Some articles (such as paper, silk, sponge, wool) are injured by chlorine : so they are always bleached by means of sulphur dioxide. Sulphur dioxide is also an *antichlor*, i. e. it removes traces of free chlorine left in goods that have been bleached by chlorine.

The Uses of sulphur dioxide are as a bleaching agent and antichlor, as a disinfectant and preventive of putrefaction and fermentation, and as an ingredient in the manufacture of sulphuric acid.

Tests.—(1) Sulphur dioxide is recognised by its smell and bleaching action.

(2) Paper moistened with potassium bichromate is turned green by sulphur dioxide.

(3) It turns paper moistened with a solution of iodic acid (or an *iodate*) and starch to a blue colour, owing to the liberation of iodine :



Composition.—The volumetric composition of sulphur dioxide may be shown in the same way as that of carbon dioxide : the same apparatus being used in this case. By burning a fragment of sulphur in a known volume of oxygen it is found (when the apparatus has cooled) that the volume of sulphur dioxide produced is equal to the volume of oxygen used. Hence, *sulphur dioxide contains its own volume of oxygen*.

Knowing the density of sulphur dioxide to be 32, it can then be easily ascertained that its formula is SO_2 .

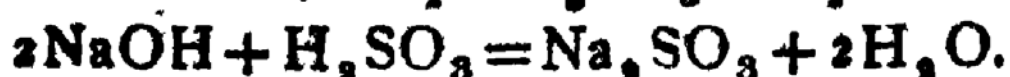
SULPHUROUS ACID, H_2SO_3 .

- This acid is produced by passing sulphur dioxide into water. The acid is known only in aqueous solution and smells of sulphur dioxide. It is very unstable, and gives off SO_2

when heated. It is a reducing agent: thus, when exposed to the air it is slowly converted into sulphuric acid—



Sulphites are the salts of sulphurous acid. They are produced by the union of sulphur dioxide with alkalies, or by the neutralisation of sulphurous acid by alkalies or carbonates. For example—

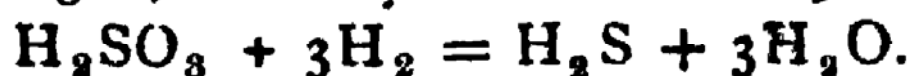


The characteristics of sulphites are the following—

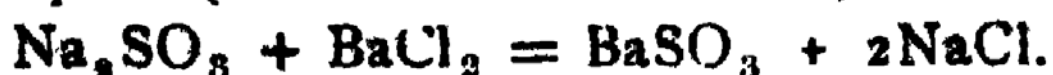
(1) When a solution of a sulphite is warmed with H_2SO_4 or HCl , sulphur dioxide is given off. Thus,



(2) Sulphurous acid and solutions of sulphites are reduced by nascent hydrogen, with the liberation of H_2S :



(3) Sulphites form with barium chloride a white precipitate of barium *sulphite* (which is *soluble* in HCl):



SULPHUR TRIOXIDE OR SULPHURIC ANHYDRIDE.

FORMULA SO_3 . MOLECULAR WEIGHT 80. VAPOUR DENSITY 40.

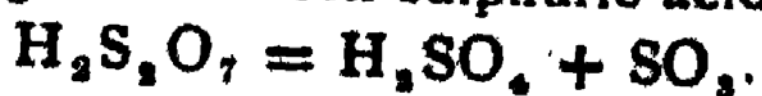
Preparation.—It is prepared as follows:

1. By passing a mixture of dry oxygen and sulphur dioxide over heated platinized asbestos or spongy platinum contained in a bulb-tube. Dense white fumes of sulphur trioxide are produced, which may be condensed in a receiver.

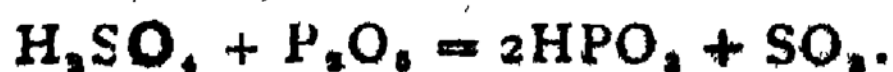


[In the above reaction, the finely-divided platinum acts as a catalytic agent. Sulphur trioxide is now being prepared on a large scale by this method, for the subsequent production of sulphuric acid. The *Contact Process*, as it is called, is expected to be a serious rival of the *Chamber Process* of manufacturing sulphuric acid, described below].

2. By heating Nordhausen sulphuric acid:



3. By heating sulphuric acid with phosphorus pentoxide (which withdraws the elements of water from the acid):



Properties.—It is a white, silky, crystalline solid which easily melts to a colourless liquid and boils at 46°C . When passed through a red-hot tube, the vapours of sulphur trioxide are decomposed into sulphur dioxide and oxygen. Sulphur trioxide is very hygroscopic: thus it fumes in the air, and unites with water energetically (with a hissing sound) to form sulphuric acid. $[\text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4]$.

SULPHURIC ACID OR HYDROGEN SULPHATE.

FORMULA H_2SO_4 . MOLECULAR WEIGHT 98.

Preparation.—The preparation of this, the most useful of the acids and the most important of all manufactured chemical substances, consists in the oxidation of sulphur dioxide in the presence of water (*i. e.*, in the oxidation of sulphurous acid). But as this oxidation cannot be directly effected by the oxygen of the air, it is brought about by an oxide of nitrogen (NO_2). Nitrogen peroxide gives up half of its oxygen to sulphurous acid to form sulphuric acid, and then replenishes its loss from the oxygen of the air.

Laboratory Method.—To prepare sulphuric acid in

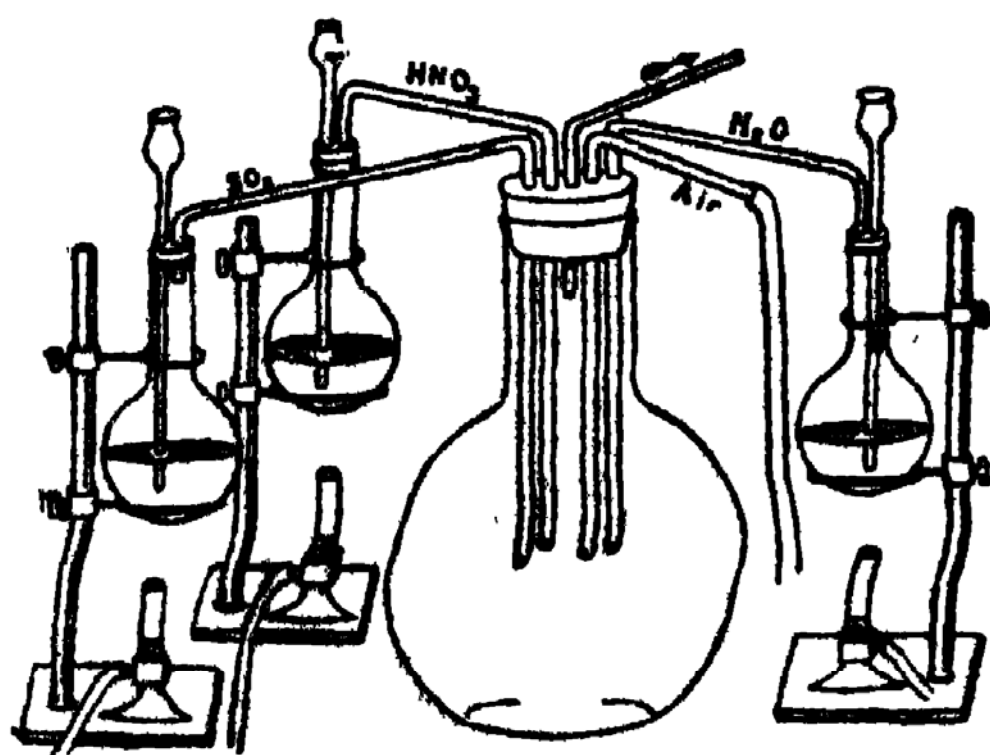


Fig. 45.

the laboratory the following method is adopted. A large flask is fitted up with five tubes, through four of which are passed — (1) Sulphur dioxide, obtained by heating sulphuric acid with copper; (2) Fumes of nitric acid, prepared from nitre and sulphuric acid; (3) Steam obtained by boiling water; (4) Pure air, of which only oxygen is required.

the laboratory the following method is adopted. A large flask is fitted up with five tubes, through four of which are passed — (1) Sulphur dioxide, obtained by heating sulphuric acid with copper; (2) Fumes of nitric acid, prepared from nitre and sulphuric acid; (3) Steam

The fifth tube is for the exit of waste gases, mainly nitrogen. When the experiment is complete, sulphuric acid is found to have collected in the flask. The following equations represent the reactions :



NO_2 produced in the first reaction oxidizes H_2SO_3 (that is, $\text{SO}_2 + \text{H}_2\text{O}$), and is itself reduced to NO which combines with the oxygen of the air to form NO_2 again. This NO_2 again acts upon H_2SO_3 and is itself changed into NO which carries oxygen once more from the air. Thus when once the action has been started by the nitric acid fumes, reactions (ii) and (iii) go on in alternation,—nitric oxide being the ‘carrier of oxygen.’

✓ **Manufacture.**—The processes employed in the manufacture of sulphuric acid are essentially the same as those described above, and the reactions are the same. The Sulphuric Acid Works, the general arrangement of which is represented here in rough outlines, consist mainly of these parts—

1. Furnace for burning iron pyrites or sulphur in order to obtain sulphur dioxide and air.
2. Nitre oven for producing nitric acid fumes.
3. Boiler for producing steam.

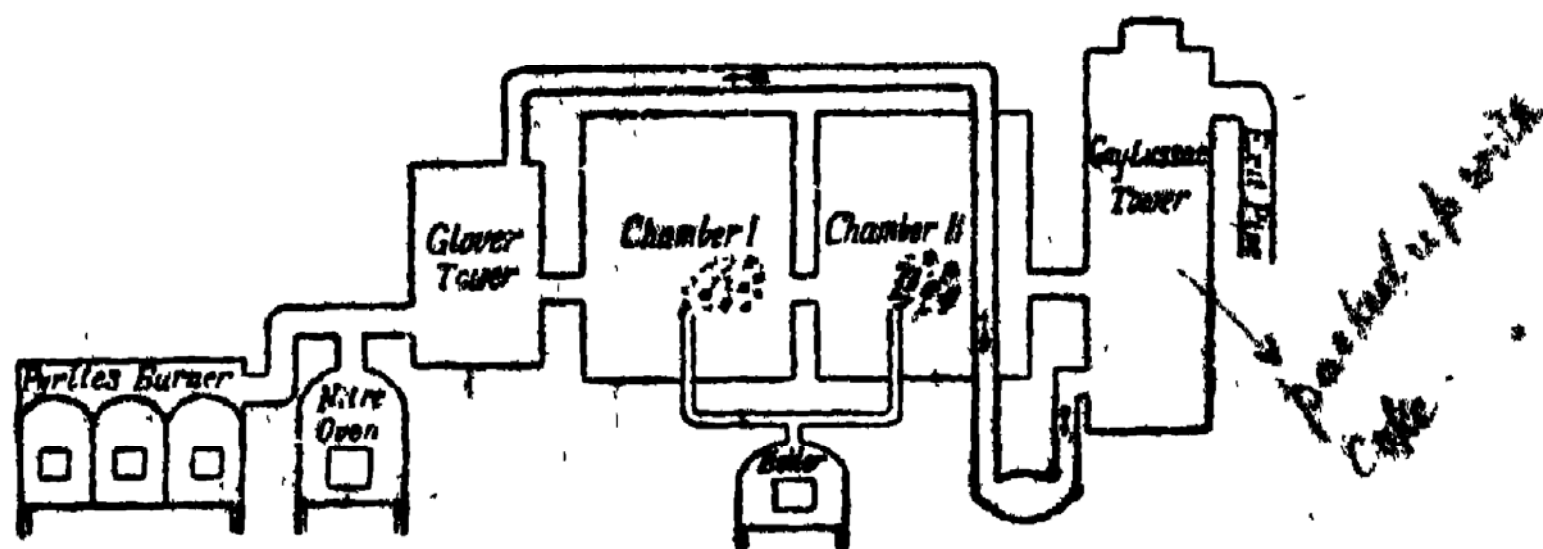


Fig. 46.

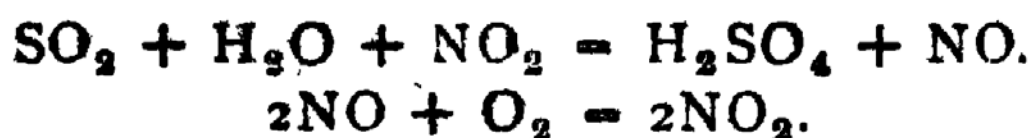
4. Chambers, made of lead and enclosed within timber frames, in which the acid is formed.

5. Gay-Lussac Tower and Glover Tower which economize the process of manufacture by respectively absorbing and restoring nitrogen peroxide which escapes with the waste gases from the chambers.

The hot gases from the burners (*vis.* sulphur dioxide, air, and nitric acid fumes) are drawn through the whole apparatus by means of a powerful draught from a chimney. The gases pass up through the Glover tower into the chambers which are supplied with steam by means of jets connected with the boiler. First the nitric fumes unite with SO_2 to form H_2SO_4 and NO_2 —



Then the reactions represented by the following equations go on alternately to form H_2SO_4 which collects at the bottom of the chambers—



✓ The unused gases (chiefly nitrogen, oxygen, and oxides of nitrogen) pass from the chambers into the Gay-Lussac tower where nitrogen peroxide is absorbed by sulphuric acid, and other waste gases are allowed to escape through the chimney. The *nitrated* sulphuric acid is then pumped to the top of the Glover tower where the absorbed nitrogen peroxide is liberated again and then returned to the chambers for fresh use.

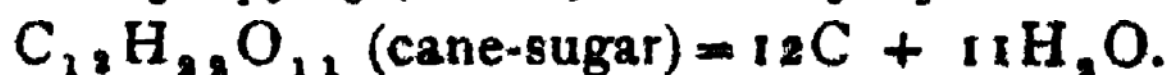
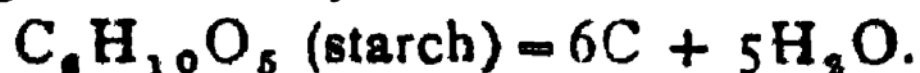
NOTE 1.—When there is want of steam in the chambers, a peculiar white crystalline compound is formed, called *chamber crystals*. These crystals are immediately dissolved by water and decomposed into sulphuric acid and oxides of nitrogen.

NOTE 2.—*Pure sulphuric acid* cannot be prepared in the chambers, because the hot concentrated acid would attack the lead of which the chambers are made. The acid obtained from the chambers contains only 68 p. c. of pure H_2SO_4 , and is called 'chamber acid.' After evaporation in leaden pans the acid acquires a specific gravity of 1.75, *i.e.* containing 81 p. c. of pure H_2SO_4 , and is commercially known as 'brown acid.' By further concentration in platinum or glass vessels the acid reaches the

strength of 98 p. c. (= specific gravity 1.842) and is then called in commerce *oil of vitriol*. The abbreviation 'B.O.V.' is sometimes used for brown oil of vitriol.

Properties: Physical.—Commercial sulphuric acid contains many impurities and is therefore more or less coloured. The pure acid is a colourless and odourless oily or syrupy liquid which is more than $1\frac{1}{2}$ times heavier than water. When cooled, it condenses to colourless crystals. When heated, it at first gives off sulphur trioxide, and then boils unchanged at $338^{\circ}\text{C}.$; but when extremely heated, it decomposes into sulphur dioxide, oxygen and water.

Chemical.—1. *The acid has great affinity for water, and is therefore used as a drying agent.* It abstracts the elements of water from organic compounds, and unites with water to form hydrates having the formulæ $(\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O})$ and $(\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O})$. Thus, it decomposes formic acid, oxalic acid, and alcohol (*Vide* pp. 150, 156); and carbohydrates (*e. g.* starch, sugar, paper, wood) are charred or blackened by the acid—water being absorbed by the acid and carbon left behind:



The acid is a powerful caustic and causes painful wounds.

2. *Sulphuric acid attacks most of the metals.* Iron, magnesium, manganese, and zinc are acted upon by the cold and dilute acid, hydrogen being evolved. Antimony, bismuth, copper, lead, mercury, silver, and tin are acted upon by the hot and concentrated acid, with the liberation of sulphur dioxide. But gold and platinum are not attacked by the acid.

Uses.—Sulphuric acid is put to varied uses in art and trade. It is required in the manufacture of hydrochloric, nitric, and other acids. By its means are prepared 'soda' (*i. e.* sodium carbonate, which is necessary in manufacturing soap and glass) and compounds of phosphorus (which are used as manures). It is also used in refining petroleum, and in voltaic batteries for producing electricity.

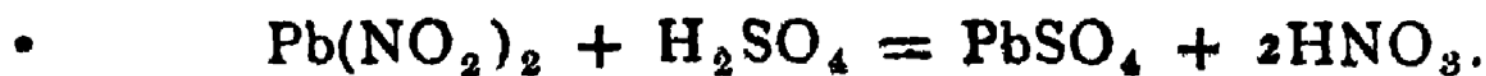
Test.—See below.

Sulphates.—These are the salts of sulphuric acid. Being a dibasic acid, sulphuric acid produces two series of salts, viz., 'normal salts' (as K_2SO_4) and 'acid salts' (as $KHSO_4$). Nearly all sulphates are soluble in water: except sulphates of calcium and strontium which are only slightly soluble, and sulphates of lead and barium which are insoluble in water and acids. The characteristic tests for sulphates are these—

(1) A solution of barium chloride, when added to a solution of a sulphate (or to sulphuric acid), produces a white precipitate of barium sulphate which is *insoluble* in dilute hydrochloric acid.



(2) Similarly, lead nitrate produces a white precipitate of lead sulphate.



(3) When a sulphate is mixed with sodium carbonate and then heated on charcoal in the reducing blowpipe flame, a *sulphide* is produced.

[The above are the tests which serve to distinguish a *sulphate* from a *sulphite*. They are also distinguished by the fact that sulphites evolve sulphur dioxide when acted on by an acid, whereas sulphates do not].

Pyrosulphuric Acid, $H_2S_2O_7$.—This may be regarded as a compound of a molecule of H_2SO_4 with a molecule of SO_3 . It is prepared in large quantities at a place in Saxony, whence it is called *Nordhausen Sulphuric Acid*. It is a fuming oily liquid, and is therefore also called *Fuming Sulphuric Acid*. When heated it gives off sulphur trioxide.

Thiosulphuric Acid, $H_2S_2O_3$.—This unstable acid forms the important salt Sodium Thiosulphate, $Na_2S_2O_3$, which is largely used in photography under the familiar name 'hyposulphite of soda' or simply *hypo*.

University Examination Questions.

I.

1. Describe the preparation of sulphur dioxide and make a sketch of the apparatus used [C. 99, 03, 1910, 1912 ; A. 05, 1910].

2. Describe the properties of sulphur dioxide [C. 99, 1912]. How would you prepare sulphur from the gas? [C. 1912]. By what properties can sulphur dioxide be distinguished from chlorine? [C. 1910]. Compare the action of chlorine on vegetable colour with that of sulphur dioxide. [C. 1913].

3. What happens when this gas is dissolved in water, and the solution thus obtained is treated with (a) chlorine water, (b) solution of caustic potash? Give equations in each case [C. 03].

What takes place when this gas is allowed to come into contact with (a) sulphuretted hydrogen, (b) lead peroxide, (c) caustic soda, (d) hydrogen dioxide? [A. 05].

4. State concisely how the composition of sulphur dioxide has been determined. Make a sketch of the apparatus required [C. 06]. How will you ascertain that the formula SO_2 represents the composition of sulphur dioxide gas? [A. 05].

5. How may sulphur and sulphur trioxide be obtained from sulphur dioxide? [A. 1910].

II.

1. Describe an experiment by means of which sulphuric acid can be prepared in the laboratory [A. 99].

Mention briefly but concisely the process by which sulphuric acid is produced, and enumerate the chief uses of the substance for industrial purposes [C. 1911].

2. Give a short account of the method employed in the manufacture of sulphuric acid [C. 1913, 16 ; A. 93, 96, 05, 06, 07, 1910]. Explain carefully the action of nitric oxide in its manufacture [A. 94, 99]. What impurities are generally present in the commercial acid, and how may they be removed [C. 1916 ; A. 05].

Draw carefully a diagrammatic sketch of the plant used for the manufacture of sulphuric acid by the 'lead chamber process.' Name each part of the plant and state its uses. How is sulphuric acid concentrated? [A. 1914].

3. Mention the principal properties of strong sulphuric acid [A. 99]. What are its properties and tests? [C. 1913].

4. Give the equations representing the action which takes

place (a) when copper, common salt, and caustic potash are treated with this acid [A. 96], (b) when strong sulphuric acid is heated with carbon, sulphur, copper, and common salt. [A. 1900]. What is the test for a sulphate? [A. 1900].

CHAPTER XXV.

PHOSPHORUS AND ITS COMPOUNDS.

SECTION I.

PHOSPHORUS.

ATOMIC WEIGHT 31. MOLECULAR FORMULA AND WEIGHT P_4 , 124.

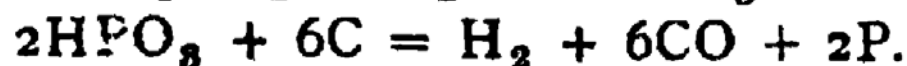
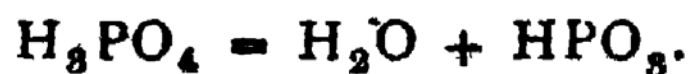
Occurrence.—Phosphorus cannot be found in the free state in nature. It occurs in combination, chiefly as calcium phosphate, (i) in the minerals *apatite* and *phosphorite*, (ii) in plants, and (iii) in the bones, brain, and urine of animals.

Preparation.—I. *Ordinary phosphorus* is prepared by the following two methods :

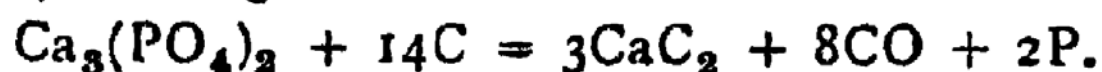
(i) Bone-ash, which is almost pure calcium phosphate $[Ca_3(PO_4)_2]$, is mixed with sulphuric acid, and is thereby decomposed into insoluble calcium sulphate and orthophosphoric acid—



The acid solution is then filtered, concentrated, and mixed with powdered charcoal. The dry mixture is heated in earthen retorts the stems of which dip under water. At first orthophosphoric acid is changed into metaphosphoric acid, which is decomposed at a high temperature by the charcoal, and phosphorus distils over—



(ii) Phosphorus is now also prepared directly from calcium phosphate by heating it with carbon in an electric furnace—



II. *Red or Amorphous phosphorus* is obtained by heating ordinary phosphorus for some days, without access of air, at a temperature between 240° and $250^\circ C$. [When heated above

260°C. the red phosphorus is again changed into ordinary phosphorus and burns].

Two Forms of Phosphorus.—Phosphorus exists in two forms, viz., Ordinary or Yellow Phosphorus and Red or Amorphous Phosphorus. These two varieties differ widely in their properties; but that they are the *allotropic modifications* of the same element is evident from the following considerations:

(i) Ordinary phosphorus can be converted by heat into red phosphorus; and when a certain weight of red phosphorus is heated again in a vessel containing carbon dioxide (so as to prevent combustion of the phosphorus), the same quantity of yellow phosphorus is produced.

(ii) Both the varieties produce, when burnt, the same weight of phosphorus pentoxide.

Properties.—Phosphorus readily combines with hydrogen, oxygen, sulphur, and the halogens. But while ordinary phosphorus is very active, red phosphorus is inert. The properties of the two varieties are in many respects reverse to each other, and are given below in parallel columns:—

<i>Ordinary Phosphorus.</i>	<i>Red Phosphorus.</i>
1. Yellowish, transparent, soft like bees'-wax: becomes hard, brittle, and crystalline at 0°.	1. Opaque, hard, and almost amorphous.
2. Specific gravity 1.8.	2. Specific gravity 2.2.
3. Insoluble in water, slightly soluble in ether, alcohol, &c., readily soluble in carbon disulphide.	3. Insoluble in all the solvents.
4. Highly poisonous.	4. Non-poisonous.
5. Melts and burns at about 44°.	5. Melts above 250° and burns at 260°.
6. Luminous in the dark (whence its name) and fumes in moist air—hence it is kept under water.	6. Non-luminous, oxidizes slowly when exposed to moist air—hence it need not be kept under water.
7. Ignites easily by friction, even by the mere handling—ordinary 'friction-matches' are prepared from it.	7. Not ignited by friction upon ordinary rough surfaces—'safety-matches' are prepared from it.
8. Acted upon by caustic soda.	8. Unaffected by caustic soda.

Uses.—Phosphorus is chiefly used in manufacturing matches. [See above].

University Examination Questions.

1. What is the chief source of phosphorus and its compounds? Give a short but clear account of the processes employed for the preparation of phosphorus from bone-ash. Represent all the reactions by equations. How could you prove that common and red phosphorus are modifications of the same element? [A. 1912].
2. How does phosphorus occur in nature? [A. 96]. Compare the different varieties of phosphorus [A. 93, 96, 08]. Explain how each allotropic form may be produced [A. 08].
3. How is phosphorus usually prepared? Give an account of its properties and of its reactions with (a) oxygen, (b) chlorine, and (c) a solution of caustic soda [A. 1911].
4. How is yellow phosphorus manufactured and purified? Compare the different varieties of phosphorus, and explain how each allotropic form may be transformed into the other [A. 1913, 15].

SECTION II.

PHOSPHORETTED HYDROGEN.

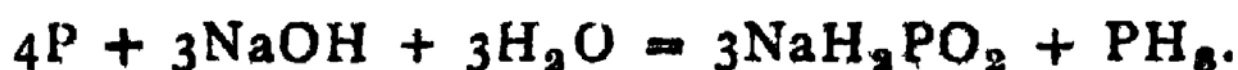
* (*Hydrogen Phosphide*).

Phosphorus unites with hydrogen in different proportions to form three phosphides, viz —

- (1) Phosphine or Gaseous phosphoretted hydrogen, PH_3 ;
- (2) Liquid phosphoretted hydrogen, P_2H_4 ; and
- (3) Solid phosphoretted hydrogen, P_4H_2 .

The molecular weight and density of phosphine is 34 and 17 respectively.

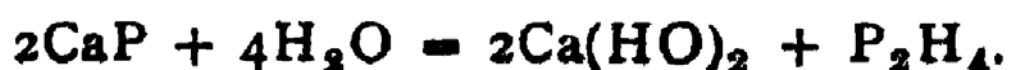
Preparation : (1) Of PH_3 .—It is prepared by heating phosphorus with a solution of caustic soda or potash :



The caustic alkali, water, and phosphorus are placed in a flask fitted up with a delivery tube which leads under water.

The air in the flask is displaced by passing a stream of coal-gas or carbon dioxide, and then the flask is gently heated. Phosphine (mixed with traces of P_2H_4) is evolved, and may be collected by displacement of water. [Care is taken that the gas may not come in contact with air. Thus as each bubble of the gas rises above the surface of water and comes in contact with air, it at once takes fire forming beautiful vortex rings of the smoke of phosphorus pentoxide].

(2) Of P_2H_4 .—This is prepared by passing phosphine (obtained by the above method or by the action of water on calcium phosphide) through a U-tube immersed in a freezing mixture. The reaction in the latter case is this—



(3) Of P_4H_2 .—Liquid phosphoretted hydrogen, when exposed to light, is at once decomposed into the gaseous and solid phosphides :



Properties.—Phosphine is colourless and has the bad smell of rotten fish. It is highly poisonous and inflammable. Like ammonia it unites with the halogen acids to form *phosphonium salts*.

Liquid phosphoretted hydrogen is colourless and burns spontaneously in contact with air. It is due to its presence in traces that phosphine takes fire spontaneously.

Solid phosphoretted hydrogen is a yellow powder.

University Examination Questions.

1. What is the formula of phosphoretted hydrogen, its molecular weight and density? Describe its preparation and properties, giving a sketch of the apparatus you would use in preparing it. [A. 02].

2. Describe carefully how you would prepare and test phosphoretted hydrogen gas [A. 1912].

SECTION III

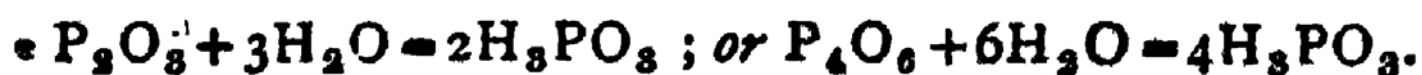
OXIDES AND OXYACIDS OF PHOSPHORUS.

Phosphorus forms four oxides and four or more oxyacids, of which the following are important—

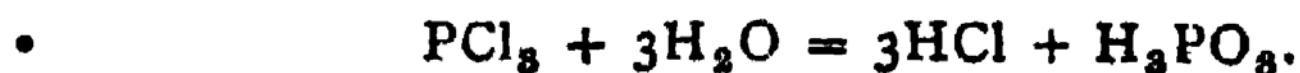
Phosphorus trioxide, giving rise to Phosphorous acid ;

Phosphorus pentoxide, giving rise to Phosphoric acid.

I. PHOSPHORUS TRIOXIDE (*Phosphorous anhydride*), P_2O_3 or P_4O_6 .—This oxide is formed when phosphorus is burned in an insufficient supply of air. It is a white solid which smells like garlic and is highly poisonous. It dissolves slowly in *cold* water, forming phosphorous acid :



PHOSPHOROUS ACID, H_3PO_3 .—This acid is readily prepared by the action of water upon phosphorus trichloride :



It is a crystalline solid having garlic-like smell. It is decomposed by heat into phosphoric acid and phosphine :



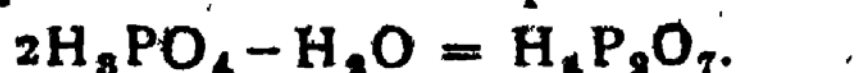
It is a great reducing agent.

II. PHOSPHORUS PENTOXIDE (*Phosphoric anhydride*), P_2O_5 .—This oxide is prepared by burning phosphorus in a sufficient supply of air or oxygen. It is a white flaky powder which readily absorbs moisture from the air. It is the most powerful of all drying agents, and unites energetically with water forming phosphoric acid :



PHOSPHORIC ACID, H_3PO_4 .—It is prepared by dissolving phosphorus pentoxide in boiling water, or by the action of sulphuric acid on bone-ash. (See preparation of phosphorus). It is a transparent, cystalline, deliquescent solid. Being tribasic it forms three series of salts, called *phosphates*. It is also called *Orthophosphoric Acid* to distinguish it from the following two acids :

(1) *Pyrophosphoric Acid*, $\text{H}_4\text{P}_2\text{O}_7$, which is obtained by heating orthophosphoric acid to a temperature of 213°C :



(2) *Metaphosphoric Acid*, HPO_3 , which is obtained by heating H_3PO_4 to redness, (or by heating $\text{H}_4\text{P}_2\text{O}_7$):



It is also called *glacial phosphoric acid*.

University Examination Questions.

1. What is the constitution of the oxide formed when phosphorus burns in the open air, and of the acids formed when the oxide combines with water [A. 93].

2. Under what conditions are the lower and higher oxides of Phosphorus formed? What acids are derived from these oxides? Describe the physical and chemical properties of H_3PO_4 . [A. 07].

CHAPTER XXVI.

SILICA, SILICATES AND GLASS.

The element silicon is never found in the free state in nature. In the combined state it occurs plentifully as silica and silicates, and it forms (next to oxygen) the most important constituent of the earth's crust.

SILICON DIOXIDE, (SiO_2) commonly called *silica*, is found in two modifications: quartz or rock-crystal and amethyst are silica in crystallised form; while agate, flint, opal, and sand are examples of amorphous silica (more or less mixed with the crystalline variety).

Silica requires the strong heat of the oxyhydrogen blow-pipe to be melted to a glass-like substance. Silica is insoluble in water and in all acids, excepting hydrofluoric acid; but it dissolves in a strong boiling solution of caustic potash or soda, and amorphous silica is also soluble in a boiling solution of an alkaline carbonate. Silica is often called *silicic anhydride*, because it forms with water a number of silicic acids.

SILICATES are the salts of silicic acids. The chief silicates are those of aluminium, calcium, and magnesium. Clay, the

purest form of which is kaolin or china-clay is a silicate of aluminium. Asbestos, hornblende, meerschaum, mica, pumice, serpentine, &c. are other important silicates occurring in nature.

Porcelain, water-glass and glass are the chief artificial silicates. Porcelain is generally prepared by mixing china-clay with felspar. *Water-glass* or *soluble glass* is prepared by fusing sand with an excess of sodium carbonate, or by boiling together silica and caustic soda or potash. Water-glass is a syrupy liquid, soluble in water; it is largely used as a protective coating for stone-work, as also in the manufacture of artificial stone, soap, &c.

GLASS consists of (1) silica, (2) soda or potash, (3) oxide of calcium or lead. The presence of sodium renders the glass 'soft,' *i. e.*, easily fusible. The presence of potassium renders the glass 'hard,' *i. e.*, difficult to melt.

Common glass (window glass, &c.) is prepared by melting together sand, sodium carbonate and lime or calcium carbonate. *Bohemian glass* contains potassium carbonate instead of sodium carbonate: it is used in the manufacture of chemical apparatus. *Flint glass* is potash glass which contains lead oxide (litharge) in the place of lime: it melts easily, takes a high polish, and is thus used for the manufacture of optical instruments.

Coloured glasses are prepared by adding different metallic oxides to glass while in the molten state. Thus cuprous oxide makes glass red, cobalt oxide makes it blue, chromium oxide makes it green, and so on.

University Examination Questions.

1. How is glass made? What is the difference between hard glass and soft glass, (a) in manufacture, (b) in behaviour? What is *soluble glass*? [A. 06].
2. What are the composition, properties and uses of glass? [A. 08].
3. Write a short essay of not more than three pages on glass. [A. 1913].

PART III.

METALS.

CHAPTER XXVII.

THE METALS.

General Characteristics of Metals.—*The physical peculiarities* of metals are that they have what is called 'metallic lustre': they are generally heavy, opaque, good conductors of heat and electricity, ductile (*i. e.*, can be drawn into fine wire), and malleable (*i. e.*, can be hammered into thin sheets).

Their chemical characteristics are that metals replace the hydrogen of acids to form salts, and generally form basic oxides, *i. e.*, oxides which neutralise acids and form salts. Metals readily form compounds with non-metals (excepting hydrogen), and are electro-positive, *i. e.*, appear at the negative electrode when their compounds are decomposed by electricity.

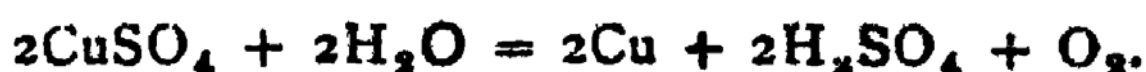
Extraction of Metals.—Only some metals, *viz.* bismuth, copper, gold, platinum, and silver, are found in the native state. All other metals occur as compounds, known as *minerals*. These compounds are also called the *ores* from which the metals are extracted.

The extraction of metals from their ores is the subject-matter of Metallurgy. Generally there are two steps in the process of extraction, *viz.*, (1) *roasting*, *i. e.*, heating the ore to red-heat in sufficient air, and (2) *reducing*. By roasting the ore we get rid of water, carbon dioxide, sulphur, &c; and thus usually the oxide of the metal is left behind. Reduction to the metallic state is effected by simple heating (as in the

cases of oxides of mercury and silver) or heating with a reducing agent, such as carbon or carbon monoxide —



A metal is also extracted by subjecting one of its salts (in a state of fusion or solution) to electrolysis or to the influence of some other suitable metal. Thus copper is obtained by electrolysing copper sulphate solution, or by placing a strip of iron in the solution—



Compounds of Metals.—These are mainly classified thus:

(1) *Oxides and Hydroxides*, i. e. compounds with oxygen and hydrogen.

(2) *Chlorides, Bromides, and Iodides*, i. e. compounds with chlorine, bromine, and iodine.

(3) *Sulphides and Hydrosulphides*, i. e. compounds with sulphur and with sulphur and hydrogen.

(4) *Chlorates, Chlorites, &c.*, i. e. salts of the oxy-acids of chlorine.

(5) *Sulphates and Sulphites*, i. e. salts of sulphuric and sulphurous acids.

(6) *Nitrates and Nitrites*, i. e. salts of nitric and nitrous acids.

(7) *Carbonates*, i. e. salts of carbonic acid.

(8) *Phosphates*, i. e. salts of phosphoric acid.

(9) *Borates*, i. e. salts of boric acid.

(10) *Silicates*, i. e. salts of silicic acid.

Preparation of Oxides and Hydroxides.—Oxides of metals are prepared (i) by heating the metals in air or oxygen, (ii) by the action of some metals on water, (iii) by heating nitrates and carbonates, and (iv) by strongly heating precipitated hydroxides.

In the case of the metals of the alkalies and alkaline earths, the hydroxides are formed by direct union of their oxides with

water. Hydroxides of the other metals are insoluble, and are obtained by precipitating solutions of the respective salts by means of an alkali.

Preparation of Salts.—See p. 89. To prepare a soluble salt, the carbonate of the metal is dissolved in the proper acid, and then the salt is obtained by filtration or decantation and evaporation. An insoluble salt is generally prepared by precipitation.

Soluble and Insoluble Salts.—All *chlorates* and *nitrates* are soluble in water. All *chlorides* (excepting those of lead and silver, and cuprous and mercurous chlorides) are soluble. *Sulphates* are also soluble (excepting those of calcium, barium, strontium, and lead). *Sulphides*, *carbonates*, and *phosphates* are insoluble (excepting those of the alkalies). *Acid salts* of soluble acids are soluble, *basic salts* are insoluble. [See Appendix].

CHAPTER XXVIII.

SODIUM AND POTASSIUM.

General Similarities.—The metal sodium and potassium (together with the metals lithium, rubidium, and caesium) form a group called the *alkali metals*. They are silvery-white, soft solids which rapidly tarnish in moist air, and decompose water at ordinary temperatures. They form strong alkaline solutions and their carbonates are soluble in water. They are monovalent, and readily unite with chlorine.

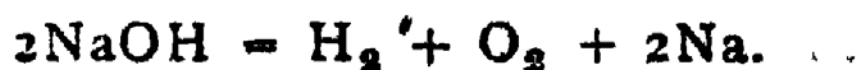
SODIUM.

SYMBOL Na. ATOMIC WEIGHT 23.

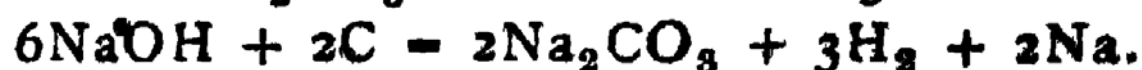
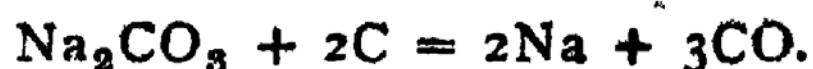
Occurrence.—On account of its strong attraction for oxygen, sodium does not occur free in nature. But the following of its compounds are found in plenty :—(1) Sodium chloride or common salt, which occurs in the solid state as *rock-salt* and in solution in sea-water; (2) Sodium nitrate, also called

Chili saltpetre or *cubic nitre*; (3) Sodium carbonate, which occurs in the ashes of sea-plants, and as crusts on the soil (called *trona* and *natron*, whence the name of the metal 'natrium' is derived).

Preparation.—(1) Davy who discovered sodium obtained it by the electrolysis of melted caustic soda.



(2) Sodium was hitherto manufactured by distilling (a) a mixture of sodium carbonate and charcoal, or (b) a mixture of powdered iron, charcoal, and caustic soda :



(3). It is now manufactured by the electrolysis of fused caustic soda or fused sodium chloride. (a) The first method, devised by Castner, is an improvement of Davy's original plan. As the result of the decomposition of caustic soda, oxygen is liberated at the anode, while sodium and hydrogen liberated at the cathode rises up into a receiver. The gases are allowed to escape, and the metal is collected. (b) The latter method is that of Borchers. In this process, sodium (produced in the cathode) immediately flows into a receiver, and chlorine gas (liberated at the anode) escapes through a pipe and is collected for its own uses.

Properties : Physical.—Sodium is a soft silver-white metal having (when freshly cut) a bright lustre. It is lighter than water, its specific gravity being 0.974 nearly. Sodium forms with potassium a liquid alloy which is used in the construction of thermometers.

Chemical.—Sodium has strong attraction for oxygen. Hence—

(a) It is kept under petroleum (which is free from oxygen).

(b) When exposed to the air, it tarnishes owing to the formation of sodium monoxide. It burns in the air with a yellow flame, forming sodium monoxide and dioxide. But perfectly dry air or oxygen has no action on sodium.

(c) It is used as a reducing agent in the preparation of aluminium and magnesium.

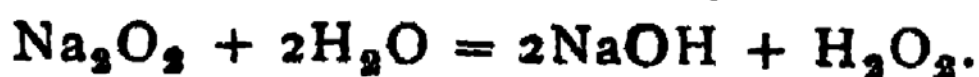
(d) When it is thrown on water, hydrogen is evolved and caustic soda formed. $[2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2]$.

Sodium and potassium dissolve in liquid ammonia.

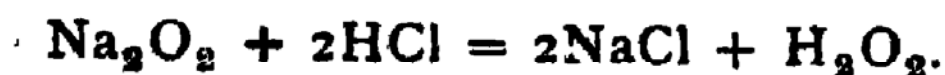
COMPOUNDS OF SODIUM.

Sodium Monoxide, Na_2O .—This is a grey solid, prepared by heating sodium to 180° in the air. It readily unites with water, forming caustic soda. $[\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}]$.

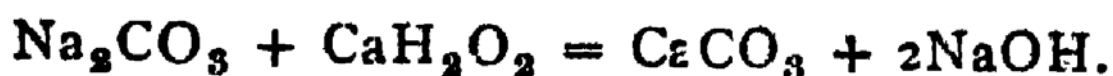
Sodium Dioxide or Peroxide, Na_2O_2 .—This is a yellowish white solid, prepared by heating sodium to about 300° in excess of air or oxygen. It is a powerful oxidizing and bleaching agent. When thrown into water, it evolves oxygen; but when cold water is used, hydrogen peroxide is formed:



When it is treated with dilute hydrochloric acid, a solution of common salt and hydrogen peroxide is formed which is largely used as a bleaching agent:

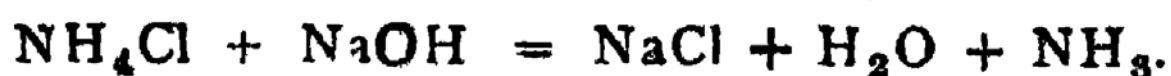


Sodium Hydroxide or Hydrate, NaOH , commonly called *caustic soda*. It is obtained (i) by the action of sodium on water, (ii) by dissolving an oxide of sodium in water. (iii) On the large scale, it is prepared by boiling (in a silver or an iron dish) a solution of sodium carbonate with slaked lime:



The clear liquid thus obtained is concentrated by evaporation and cast into sticks. (iv) It is now also manufactured by the electrolysis of brine (*i.e.* a solution of common salt in water). There are several types of the electrolytic process, in all of which chlorine (evolved at the anode) is collected for making bleaching-powder, while the sodium (liberated at the cathode) unites with water to form sodium hydroxide.

Caustic soda is a white, *deliquescent, strongly alkaline* solid which corrodes the skin and absorbs carbon dioxide rapidly (p. 149). Thus when exposed to the air, caustic soda at first becomes liquid and then solidifies (owing to the formation of sodium carbonate). It liberates ammonia gas from ammonium salts, and its aqueous solution precipitates less soluble bases of metals from solutions of their salts; *e. g.*—



Caustic soda is soluble in alcohol, and is extensively used in the manufacture of soap, paper, &c.

Sodium Chloride, NaCl.—Common salt occurs in large masses as *rock-salt* at Stassfurt, in Lancashire, and other places where it is dug out of mines. It is also obtained by evaporating sea-water and the water of artificial saline springs or wells. In warm countries the evaporation is effected by exposing brine in flat basins to the sun's heat. In temperate regions, the brine is dripped over 'ricks' or piles of brushwood or twigs: the liquid thus concentrated by the action of the wind, is then boiled, whereby crystals of the salt are obtained. *Pure sodium chloride* is obtained by passing hydrochloric acid gas into a saturated solution of common salt: the sodium chloride (which is less soluble in the acid than in water) is thereby precipitated, while impurities remain in solution.

Sodium chloride forms anhydrous crystals; but frequently the presence of magnesium chloride renders common salt hygroscopic. It is almost equally soluble in hot and cold water.

Besides being a necessary article of food, common salt is valued as a preservative of fish and meat and is the basis of the preparation of all sodium compounds and of all chlorine compounds as well as of the elements themselves.

Sodium Carbonate, Na₂CO₃, commonly called *soda*. It forms crystals having the composition (Na₂CO₃ · 10H₂O); but when exposed to the air, it loses water and falls to powder.

It dissolves in water, giving an alkaline solution. It is essential to the manufacture of soap and glass, and is largely used to soften water for washing purposes. Hence its name 'washing-soda.'

Originally it was prepared from the ashes of sea-plants. But now it is manufactured by the following three methods.

The Leblanc Method.—It consists of three processes :

(i) *Salt-cake Process.*—Common salt and sulphuric acid (in required proportions) are heated in an iron-pan (*P* in Fig. 47). The resulting acid sodium sulphate (NaHSO_4) together with the unchanged so-

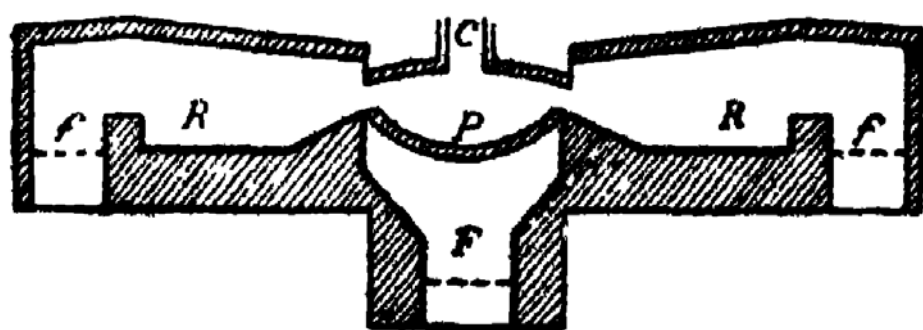


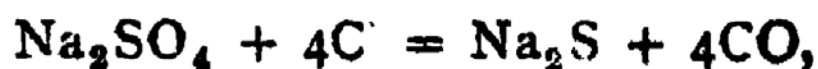
Fig. 47.

dium chloride is then raked on to the hearth of the roasters (*R, R*) where it is strongly heated by the flames from the furnaces (*f, f*) and is converted into sodium sulphate ('salt-cake'). The two reactions involved are these—



[The evolved hydrochloric acid gas passes up the flue (*c*) and is dissolved in water to form commercial hydrochloric acid].

(ii) *Black-ash Process.*—The sodium sulphate is then strongly heated with powdered coal and limestone (CaCO_3) in a reverberatory furnace: the following two reactions take place simultaneously, and a mixture of sodium carbonate and calcium sulphide ('black-ash') is finally obtained—



(iii) *Lixivation.*—The black-ash is then boiled with water; whereby the insoluble calcium sulphide is deposited, and a solution of sodium carbonate is obtained. This solution is then poured off and evaporated, till it crystallizes on cooling.

The Ammonia-Soda or Solvay Method.—In this method brine (*i.e.*, an aqueous solution of common salt) is first saturated with ammonia, and then carbon dioxide is passed into the ammoniacal liquid under pressure of about two atmospheres. Sodium bicarbonate and ammonium chloride are formed—



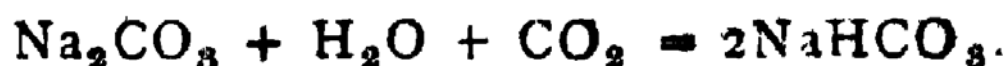
Sodium bicarbonate being less soluble is precipitated from the solution; it is then filtered off and converted by heat into sodium carbonate—



The evolved carbon dioxide and the ammonia (recovered from NH_4Cl by heating it with lime) are used over again.

The Electrolytic Method.—Sodium carbonate is now also manufactured by causing electrolytically prepared sodium hydroxide to combine with carbon dioxide.

Sodium Bicarbonate, NaHCO_3 .—It is prepared in the Ammonia-Soda process as described above, or by passing carbon dioxide into a saturated solution of sodium carbonate—



When heated, it gives off carbon dioxide. It is largely used in medicine, and is an ingredient of baking-powder.

Sodium Sulphate, Na_2SO_4 .—It is commonly known as *Glauber's salt*, and is used in medicine as a purgative. It is usually obtained (i) by the 'salt-cake process' as above described. It is also prepared (ii) by conducting a mixture of sulphur dioxide, air and water over heated sodium chloride (Hargreave's method), and (iii) by the double decomposition of magnesium sulphate and sodium chloride—



It unites with ten molecules of water to form efflorescent crystals ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

Sodium Nitrate, NaNO_3 .—Known as *Chili saltpetre* or *cubic nitre*, it occurs in large quantities in South America. As

it absorbs moisture from the air, it cannot be used in the manufacture of gunpowder. Nitric acid and potassium nitrate are prepared from it.

Tests for Sodium.

1. Sodium is distinguished by the characteristic yellow line present in its spectrum.

2. When a sodium salt is introduced on a loop of platinum wire into a Bunsen flame, the flame is coloured intensely yellow.

University Examination Questions.

1. Compare the physical and chemical properties of *sodium*, *iron* and *mercury* [C. 1912].

2. How is caustic soda prepared? State its properties? What happens when a solution of caustic soda is added to a solution of (a) potassium nitrate, (b) zinc sulphate, and (c) ammonium chloride? [C. 1910]. How is caustic soda prepared on a manufacturing scale? Describe its properties and its chief uses in the arts and in the laboratory [C. 1913, 16]. What happens when a solution of caustic soda is added to (a) calomel; (b) corrosive sublimate; and (c) blue vitriol? [C. 1913].

3. Write what you know about *sodium chloride*—the various sources from which it is obtained, methods employed for obtaining it, its properties, reactions, and uses. [C. 1912].

How are the following substances prepared from sodium chloride?—(a) sodium carbonate, (b) caustic soda, (c) hydrochloric acid [A. 1910].

4. Describe any method which you know of preparing sodium carbonate from common salt. [A. 02]. Describe fully the manufacture of sodium carbonate. [A. 06]. How is carbonate of soda commercially prepared? State its properties, and indicate its chief laboratory and industrial uses. [C. 1911].

POTASSIUM.

SYMBOL K. ATOMIC WEIGHT 39.

Occurrence.—Potassium does not exist in the free state in nature, but its compounds are widely distributed. Land-

plants contain various potassium compounds, and their ashes (called *wood-ash* or *pearl-ash*) yield potassium carbonate. Other natural compounds of potassium are the following:—(1) *Felspar*, a double silicate of aluminium and potassium, (2) *Carnallite*, a double chloride of magnesium and potassium, and (3) *Nitre* or *saltpetre*.

Preparation.—Potassium is obtained (1) by the electrolysis of fused caustic potash, (2) by distilling potassium carbonate with charcoal, or (3) by distilling a mixture of powdered iron and charcoal with caustic potash. [Compare preparation of sodium]

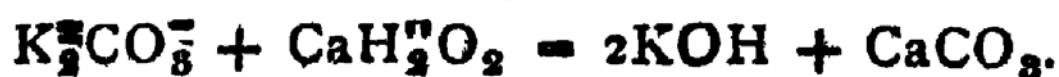
Properties : Physical.—Potassium is a lustrous, white, soft metal. Its specific gravity is 0.87.

Chemical.—*Potassium has strong affinity for oxygen.* When heated in the air, it burns with a violet light. Its bright surface rapidly tarnishes when exposed to the air; it is therefore kept under mineral naphtha. It acts upon water with great energy, causing the ignition of the liberated hydrogen and the formation of caustic potash. Potassium forms an explosive compound with carbon monoxide, and explodes violently with sulphuric and hydrochloric acids.

COMPOUNDS OF POTASSIUM.

Oxides of Potassium.—There are several oxides of potassium of which the monoxide (K_2O) and the peroxide (KO_2) are the chief. These readily unite with water forming caustic potash.

Potassium Hydroxide, KOH.—Commonly called *caustic potash*, it is formed when potassium acts upon water. It used to be prepared by boiling a solution of potassium carbonate with slaked lime—



It is now obtained by electrolysis of a solution of potassium chloride. [See preparation of caustic soda].

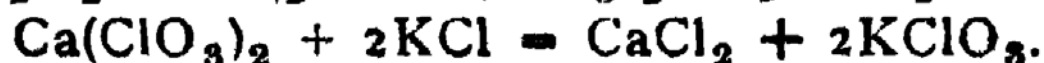
Potassium hydrate is a white solid having strong alkaline and caustic properties. It has great affinity for water and absorbs carbon dioxide, so that when exposed to the air, it is converted into a concentrated solution of potassium carbonate (*Cf.* the behaviour of caustic soda). It is used in the manufacture of soaps.

Potassium Chloride, KCl.—It is obtained from deposits of *carnallite* ($\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$). It may also be prepared by the action of hydrochloric acid on potassium carbonate. It is a deliquescent soluble salt.

Potassium Chlorate, KClO_3 .—It is obtained by passing chlorine into a *strong* and *heated* solution of caustic potash :



On the large scale, it is prepared by passing chlorine into calcium hydrate, and then adding to the resultant solution the required quantity of potassium chloride—



It is now also manufactured by electrolyzing potassium chloride solution. Potassium chlorate is found in white crystals. It is decomposed by heat, and is a powerful oxidizing agent. Its mixture with sulphur or red phosphorus explodes by friction or percussion. Hence its use in the manufacture of matches and fireworks.

[Potassium Bromide (KBr) and Iodide (KI).]—These are prepared, as in the case of potassium chlorate, by adding bromine or iodine to caustic potash. Both are soluble salts and are chiefly used in medicine and photography. Potassium iodide is a good solvent for iodine.]

Potassium Carbonate, K_2CO_3 .—It may be obtained by evaporating the solution of wood-ash. It is now generally prepared from potassium chloride by a process similar to the Leblanc Method. It is a very deliquescent salt (*Cf.* sodium carbonate which effloresces), easily soluble in water, and having alkaline properties. When carbon dioxide is passed through

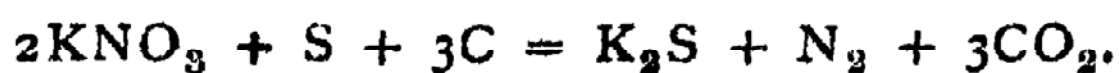
a cold saturated solution of this salt, potassium bicarbonate (KHCO_3) is formed. [See p. 149].

Potassium Sulphate, K_2SO_4 .—This salt is prepared by the action of sulphuric acid on potassium carbonate or nitrate or chloride.



Potassium Nitrate, KNO_3 .—Commonly called *nitre* or *saltpetre*, is found in hot countries as an incrustation on the earth, as a result of the oxidation of nitrogenous organic matter in the presence of the potash in the soil. This formation of nitre is called 'nitrification.' It is now prepared by treating sodium nitrate with potassium chloride. It is chiefly used in the manufacture of nitric acid and gunpowder.

Gunpowder.—This consists of charcoal, sulphur, and nitre. When the gunpowder is fired, the nitre is decomposed: its nitrogen is set free, the oxygen unites with carbon to form carbon dioxide, and the potassium unites with sulphur to form potassium sulphide (K_2S) which when blown out appears as smoke—



The heat produced is very great, about 2200° ; and the explosion is caused by the sudden expansion of the gases.

Tests for Potassium.

Dry Tests.—1. Potassium has two characteristic lines in its spectrum, one red and the other violet.

2. When a potassium salt is introduced on a loop of platinum wire into a Bunsen flame, a lavender or violet tint is imparted to the flame. [When sodium is also present in the salt, the violet tinge of potassium is masked by the yellow colour of sodium: in such cases a blue glass must be used, through which the violet flame alone is visible].

Wet Tests.—1. When a little platinic chloride is added to a solution of potassium chloride, a yellow precipitate (of the double chloride, $\text{PtCl}_4, 2\text{KCl}$) will be formed.

2. When a strong solution of tartaric acid is added to a solution of a potassium salt, and the mixture is shaken or stirred, a white crystalline precipitate (of acid potassium tartrate) will be formed.

University Examination Questions.

1. How is potassium prepared? What are its physical and chemical properties? Name and prepare the halogen compounds of Potassium and Sodium. [A. 09.]

2. Starting from potassium carbonate how would you prepare (1) nitre, (2) caustic potash? What weight of caustic potash should be obtained from 69 grams of potassium carbonate? [A. 10].

CHAPTER XXIX.

CALCIUM, STRONTIUM, BARIUM.

General Similarities.—The metals calcium, strontium and barium are called *metals of the alkaline earths*, and exhibit marked resemblances with one another. (i) All of them have a white colour and are heavier than water. (ii) They are never found in nature in the free state, being tarnished by exposure to damp air. (iii) They form oxides which behave alike as regards solubility, alkalinity and causticity. (iv) All of them decompose water at ordinary temperatures. (v) They all form insoluble carbonates.

CALCIUM.

SYMBOL Ca. ATOMIC WEIGHT 40.

Occurrence.—The chief natural compounds of the metal are (1) the carbonate (CaCO_3) in the form of *calcspar*, *chalk*, *limestone*, *marble*, *coral*, &c; (2) the sulphate (CaSO_4) in the form of *anhydrite* and *gypsum*; (3) the fluoride (CaF_2) as *fluorspar*; and (4) the phosphate, as *apatite* and *phosphorite*, as also bones of animals.

Preparation.—The metal is obtained (i) by the electrolysis of fused calcium chloride, or iodide, or (ii) by heating calcium iodide with sodium:



Properties.—Calcium is a soft silver-white metal. It tarnishes in contact with moist air and decomposes water, as sodium does. It burns when heated in the air.

COMPOUNDS OF CALCIUM.

Calcium Oxide, CaO , commonly called *lime* or *quicklime*. It is prepared by heating limestone or mollusk shells.



On the large scale, it is prepared in specially constructed egg-shaped furnaces, called *lime-kilns*, in which either (i) limestone is fed from the top and heated at the side near the bottom, or (ii) limestone and coal are thrown in alternate layers, the product being in both cases withdrawn at the bottom. A free passage of air is allowed into the kiln and the heat is carefully regulated.

Lime is an infusible substance: when heated in the flame of the oxy-hydrogen blowpipe it emits an intensely brilliant light called *lime-light*. It absorbs moisture and carbon dioxide from the air, and unites energetically with water.

Calcium Hydroxide, $\text{Ca}(\text{HO})_2$, commonly known as *slaked lime*. When water is added to quicklime, much heat is evolved and calcium hydrate is formed. This process is called *slaking*.

Slaked lime is a white powder moderately soluble in water. A thick solution of slaked lime is called *milk of lime*. The saturated solution, called *lime water*, has all the properties of an alkali and is used as a test for carbon dioxide.

Slaked lime is a good disinfectant and manure, and is used in the preparation of mortars, cements, glass, bleaching-powder, &c. The 'setting' of mortar is due to the combination of slaked lime with carbon dioxide of the air to form calcium carbonate.



Calcium Chloride, CaCl_2 .—It is prepared by dissolving chalk or marble in hydrochloric acid, and then evaporating the solution—



It is also obtained as a bye-product in the manufacture of ammonia and in the Ammonia-Soda Process.

It occurs in colourless, deliquescent crystals ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$); but when heated to 200° it loses most of its water and forms a porous mass known as 'fused chloride of calcium.' In this anhydrous form it is highly hygroscopic, and is used in drying gases (excepting ammonia with which it forms a compound). Calcium chloride crystals are very soluble in water, and form a freezing mixture when mixed with ice.

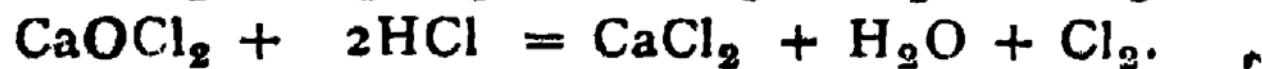
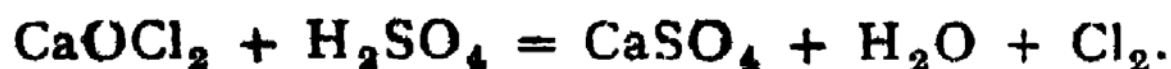
Bleaching-powder or Chloride of Lime, CaOCl_2 .—It is prepared by passing chlorine over slaked lime. There are two theories with respect to its composition: it was formerly regarded as a mixture of calcium chloride and calcium hypochlorite, formed as represented by the equation—



The modern theory is that bleaching-powder is free from calcium chloride, and is formed thus—



Bleaching-powder slowly gives up its chlorine when exposed to the air (owing to the action of carbonic acid gas). It is therefore used as a disinfectant. The addition of an acid to it causes a rapid evolution of chlorine; this fact is made use of in bleaching operations.



Calcium Carbonate, CaCO_3 .—This compound is found in nature in various forms. It may be prepared by the action of carbon dioxide on lime or by precipitating calcium chloride with an alkaline carbonate, *e. g.*—



Calcium carbonate is nearly insoluble in water.

Calcium Sulphate, CaSO_4 .—In the pure state it is found in nature as *anhydrite*. Gypsum (of which there are several varieties) contains two molecules of water. When heated, gypsum loses its water and forms a powder called *Plaster of*

Paris. A paste of Plaster of Paris with water 'sets' to a hard mass. It is therefore used in making casts. Gypsum is also a very good fertiliser. Calcium sulphate is slightly soluble in water, and its presence renders the water 'hard.'

Tests for Calcium.

Dry Reaction.—Salts of calcium, when moistened with hydrochloric acid, impart an orange-red colour to the Bunsen flame.

Wet Reactions.—Ammonium carbonate or oxalate gives, with solutions of calcium salts, a white precipitate of calcium carbonate or oxalate.

University Examination Questions.

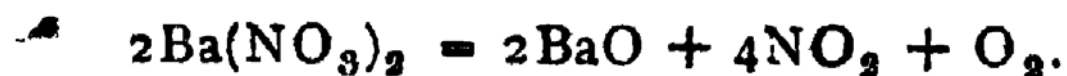
1. Compare and contrast the properties of the alkali metals with those of the alkaline earths, making particular reference to the periodic table [A. 1915].
- 2. How is marble converted into quicklime? Describe the effects of adding (a) hydrochloric acid, (b) water, to each of these substances, and state the conclusions to which these experiments lead. [C. 1910].
- 3. Distinguish between *quicklime* and *slaked lime*. How are they prepared on a large scale and what are their principal uses? How would you prepare a sample of pure anhydrous calcium chloride from either of them? What are the principal uses of fused calcium chloride in the laboratory? [C. 1912].
4. Describe the process of manufacture of quicklime. How would you prepare the chloride, the sulphate, and the carbonate of lime from the oxide? State the different uses to which the above salts are put in the laboratory and in the arts. [C. 1914].
- 5. Explain how the molecular formula for the oxide, hydroxide and chloride of calcium have been determined. [C. 1911].

{ STRONTIUM (Sr), atomic weight 87.6.
 { BARIUM (Ba), atomic weight 137.4.

- These metals closely resemble calcium. They are prepared by electrolysing their fused chlorides. The natural compounds of the metals are their carbonates and sulphates—

strontianite (SrCO_3), *witherrite* (BaCO_3), *celestine* (SrSO_4), and *barytes* or *heavy spar* (BaSO_4). The other important salts are the chlorides and nitrates. The former, SrCl_2 and BaCl_2 , are prepared by dissolving the natural carbonates in hydrochloric acid; and the latter are produced by dissolving the natural carbonates in dilute nitric acid. Barium nitrate may also be prepared by mixing hot saturated solutions of barium chloride and sodium nitrate. $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ are chiefly used in pyrotechny for the production of red and green fire respectively.

The oxides of the metals are the monoxides and the dioxides. The monoxides, SrO and BaO , are commonly known as *strontia* and *baryta*, and are prepared by heating the nitrate or the carbonate of the metals.



When the monoxides are treated with water, heat is evolved, with the formation of the hydroxides (SrH_2O_2 and BaH_2O_2) which are similar in properties to calcium hydroxide. Strontium hydroxide is used in sugar-refining.

When baryta is heated in a stream of air or oxygen, barium dioxide (BaO_2) is formed, which when further heated is reduced to the monoxide. It is used in preparing oxygen and hydrogen peroxide.

Tests for Strontium and Barium.

Dry Reactions.—Salts of strontium (moistened with hydrochloric acid) impart a crimson colour to the Bunsen flame. Salts of barium tinge the flame yellowish green.

Wet Reactions.—1. Strontium and barium salts give, with calcium sulphate or sulphuric acid, white precipitates of strontium sulphate and barium sulphate respectively. The latter is formed immediately and is insoluble in water, acids, and alkalies. Strontium sulphate is feebly soluble in water and dilute acids, but dissolves in boiling solutions of alkaline carbonates.

2. Solution of potassium chromate gives, with barium salts, a yellow precipitate of barium chromate (which is soluble

in hydrochloric and nitric acids). This test affords the distinction among calcium, strontium and barium.

University Examination Questions.

1. Explain carefully how you would prepare a sample of pure barium nitrate from barium chloride. Give full details of all operations you would perform. [A.1911].

2. Describe shortly in what manner the sulphates of barium strontium, calcium, and lead differ from each other with regard to their solubility in water, and their respective behaviour with various other solvents.

CHAPTER XXX.

MAGNESIUM AND ZINC.

General Similarities.—Magnesium, zinc, and cadmium form a group having many properties in common. All these metals are white, volatile at high temperatures, tarnish by exposure to moist air, and burn with a bright flame. They are divalent, dissolve in dilute acids and form similar compounds. Magnesium and zinc decompose water only at high temperatures.

MAGNESIUM.

SYMBOL Mg. ATOMIC WEIGHT 24.2.

Occurrence.—Magnesium occurs plentifully in nature in a state of combination. Its chief natural compounds are (i) *magnesite* (MgCO_3) and *dolomite* (a double carbonate of magnesium and calcium); (ii) *kieserite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$); (iii) *carnallite* (a double chloride of magnesium and potassium); (iv) *talc*, *hornblende*, *asbestos*, &c. which are essentially magnesium silicates.

Preparation.—It was formerly prepared by heating in a crucible a mixture of magnesium chloride and sodium. Now it is manufactured by electrolysis of fused carnallite.

Properties.—See above. Magnesium is a white, ductile, malleable metal. Its specific gravity is 1.7. It melts at

a red heat, and when heated in the air it burns with a dazzling light with the formation of the oxide. Hence its use in signalling, photography, and pyrotechny. It readily decomposes dilute sulphuric and hydrochloric acids with the evolution of hydrogen. It decomposes water slowly at boiling temperature. When heated in nitrogen, magnesium unites with it to form magnesium nitride (Mg_3N_2).

COMPOUNDS OF MAGNESIUM.

Magnesium Oxide or Magnesia, MgO .—It is a white, infusible powder, and is generally prepared by heating magnesium carbonate. It dissolves in water with difficulty, forming *Magnesium Hydroxide*, $\text{Mg}(\text{HO})_2$.

Magnesium Chloride, MgCl_2 .—It occurs in *catnallite* and in sea-water. As crystals having the composition ($\text{MgCl}_2, 6\text{H}_2\text{O}$) it may be obtained by dissolving the metal magnesium (or its oxide or carbonate) in hydrochloric acid. These crystals are partly decomposed by heat into magnesium oxide and hydrogen chloride.

To obtain the anhydrous chloride we have to add ammonium chloride to the solution of magnesium chloride: on evaporation and ignition ammonium chloride volatilises and dry white crystals of magnesium chloride are left behind. It is deliquescent and soluble in water.

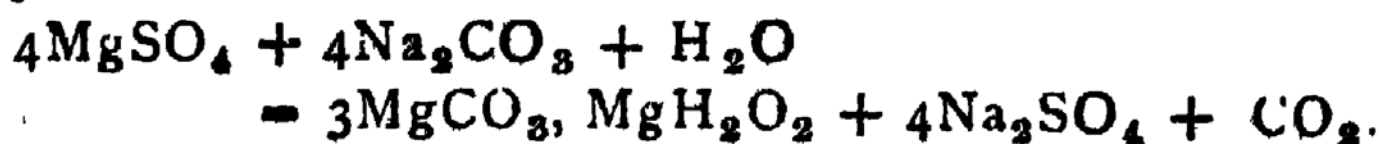
Magnesium Sulphate, MgSO_4 .—Originally it was prepared by dissolving magnesium carbonate in dilute sulphuric acid—



Thus prepared, magnesium sulphate forms soluble crystals having the composition ($\text{MgSO}_4, 7\text{H}_2\text{O}$) and is known as *Epsom salts*. Now it is obtained from the natural compound *kieserite* ($\text{MgSO}_4, \text{H}_2\text{O}$) which is only slightly soluble. It is used in medicine as a purgative.

Magnesium Carbonate, MgCO_3 .—It occurs in nature as *magnesite* and is also found in *dolomite*. What is commonly called magnesium carbonate (*magnesia alba*) is a mixture of

the normal carbonate and magnesium hydrate in varying proportions; it is prepared by mixing solutions of magnesium sulphate and sodium carbonate—



Tests for Magnesium.

Dry Reaction.—Salts of magnesium when strongly heated on charcoal before the blowpipe, give a white mass (*i. e.*, magnesium oxide) which becomes pink when moistened with cobalt nitrate and heated again.

Wet Reactions.—1. When sodium phosphate is added to a solution containing a magnesium salt together with ammonium chloride and ammonia, a white precipitate is formed.

2. Salts of magnesium are not precipitated by ammonium carbonate in the presence of ammonium chloride; whereas, under such circumstances, the salts of calcium, strontium, and barium are precipitated.

University Examination Questions

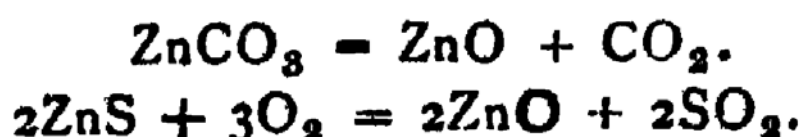
Name the natural ores of magnesium. State the properties and uses of magnesium. How would you test for magnesium in magnesia by the dry and wet methods? How would you prepare anhydrous magnesium chloride? [C. 1914.]

ZINC.

SYMBOL Zn. ATOMIC WEIGHT AND MOLECULAR WEIGHT 65.37.

Occurrence.—Zinc is found chiefly in the natural compounds *calamine* or *zinc-spar* (ZnCO_3) and *zinc-blende* (ZnS).

Preparation.—Zinc is extracted from either of the above ores. The ore is at first roasted in the air to be converted into zinc oxide—



The oxide is then reduced to the metal by heating with charcoal or coal in tube-shaped clay retorts—



The vapours of the metal are now condensed in iron receivers attached to the clay pipes. The metal thus prepared (known in commerce as *spelter*) generally contains some impurities. It is purified by repeated distillation.

Properties: Physical.—Zinc is a bluish white crystalline metal. Its physical properties vary at different temperatures—when cold it is brittle, between 100° to 150° it is ductile and malleable, above 200° it is brittle again and can be powdered, at 430° it melts, and further heated in the air it burns with a bluish white flame producing zinc oxide.

Chemical.—Zinc does not oxidise in dry air, but in moist air it tarnishes *superficially*. Pure zinc is very slowly acted upon by the acids, owing to a protective layer of condensed hydrogen being formed on the surface of the metal. But commercial zinc readily dissolves in the common acids with the evolution of hydrogen. Zinc liberates nitrous oxide from dilute nitric acid, and ammonia from the concentrated acid (p. 134). Zinc also acts upon boiling solutions of caustic soda and potash, forming the zincate and liberating hydrogen (p. 102).

Uses of Zinc.—Zinc is used for 'galvanizing' iron, for making batteries, alloys (*i. e.* mixtures of metals), &c. *Galvanized iron* is iron covered with a thin coating of zinc. *Brass* and *Dutch metal* are alloys of zinc and copper. *German silver* is an alloy of zinc, copper, and nickel.

COMPOUNDS OF ZINC.

Zinc Oxide, ZnO .—It is found in nature as *red zinc ore*, the red colour being due to the presence of manganese. It is obtained as soft flakes (formerly called *philosopher's wool*) by burning the metal zinc in air. It is also prepared by heating zinc carbonate. Zinc oxide is white when cold, but yellow when hot. Under the name *zinc-white* it is used as a paint; unlike white-lead, it is not blackened by the sulphuretted hydrogen present in the air.

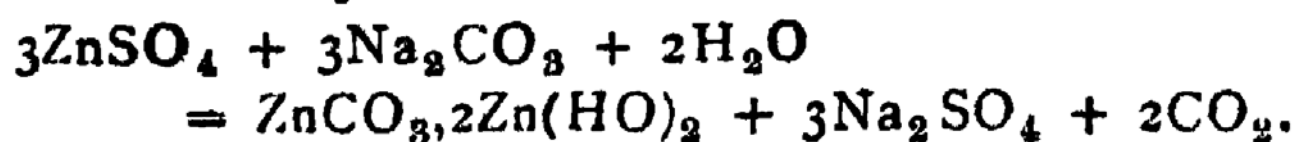
Zinc oxide does not dissolve in water to form *zinc hydroxide*

(ZnH_2O_2) which is therefore prepared by adding soda or potash to a solution of zinc sulphate.

Zinc Chloride, ZnCl_2 .—It is a white deliquescent solid, prepared by the action of hydrochloric acid on zinc. It is a powerful dehydrating caustic and poisonous substance. As a disinfectant it is used under the name of *Burnett's fluid*.

Zinc Sulphate, ZnSO_4 .—It is obtained in the preparation of hydrogen from zinc and sulphuric acid. It is manufactured by roasting zinc-blende: the sulphide is partly converted into sulphate which is separated by means of water. Zinc sulphate forms colourless efflorescent crystals ($\text{ZnSO}_4, 7\text{H}_2\text{O}$), and is called *white vitriol*. It is used as a medicine and in calico-printing.

Zinc Carbonate, ZnCO_3 .—It occurs in nature as *calamine*. It may be prepared as a basic carbonate (*i. e.*, a double carbonate and hydrate) by mixing solutions of sodium carbonate and zinc sulphate—



It is a white insoluble solid.

Tests for Zinc.

Dry Reaction.—When a zinc salt is heated on charcoal before the blowpipe, it leaves a residue of zinc oxide which is yellow while hot, but becomes white on cooling. This when moistened with cobalt nitrate and reheated, becomes bright green.

Wet Reaction.—1. Ammonium sulphide gives, with the solution of a zinc salt, a white precipitate of zinc sulphide.

2. Caustic soda or potash or ammonium hydrate gives, with the solution of a zinc salt, a white precipitate which is readily soluble in excess of the alkali.

University Examination Questions.

1. Mention the principal ores of zinc, and state how the metal is obtained. Describe the properties and the chief uses of zinc.

[C. 1913, 16]. What tests would you employ to detect zinc in sulphate of zinc? [C. 1913]. Give one dry and two wet tests for zinc [C. 1916].

3. What is the action of acids and alkalies on zinc? Describe the preparation of zinc chloride and zinc sulphate, and give their properties [A. 1913].

CHAPTER XXXI.

MERCURY.

SYMBOL Hg. ATOMIC AND MOLECULAR WEIGHT 200.

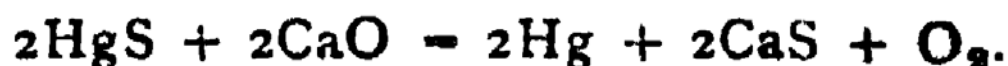
Occurrence.—Mercury is occasionally found native, but chiefly occurs as *cinnabar* (sulphide of mercury).

Preparation.—(1) Mercury is obtained by roasting cinnabar in a current of air. The resultant vapour of mercury is condensed in chambers, while the sulphur dioxide passes out.



Mercury thus obtained contains impurities. It is purified by filtering it through chamois-leather and then by shaking it with dilute nitric acid, or preferably, by distilling it in vacuo.

(2) It is also obtained in the above way by heating cinnabar with quicklime :



Properties : Physical.—Mercury is the silver-white lustrous liquid metal ; hence it is also called *quicksilver*. It solidifies at -39° and boils at 357° . Its specific gravity is 13.6. Mercury is mono-atomic.

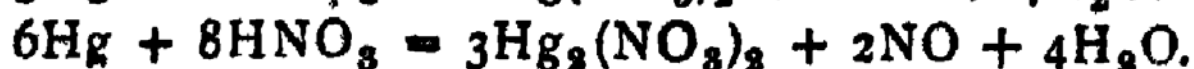
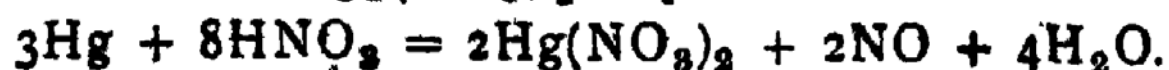
Chemical.—Mercury does not change in the air at ordinary temperatures ; but when heated above 300° it oxidizes, forming red oxide of mercury. Mercury readily unites with the halogens and sulphur. It also unites with the metals (excepting iron and platinum), forming alloys called *amalgams*. It is therefore stored in iron bottles.

Action of Acids upon Mercury.—Hydrochloric acid has no action on mercury. Strong and hot sulphuric acid dissolves

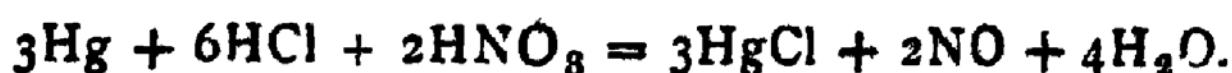
mercury, with the formation of mercuric sulphate and evolution of sulphur dioxide :



Strong and hot nitric acid rapidly acts on it forming mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$. When the dilute cold acid is used, mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$ is produced :



Aqua Regia dissolves mercury, with the formation of mercuric chloride :

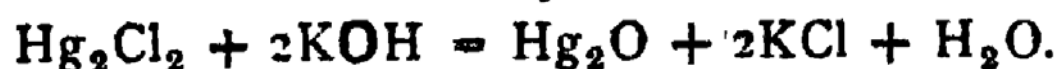


Uses of Mercury.—Besides its extensive use in medicine, mercury is used in silvering mirrors, in constructing barometers, thermometers, &c., in collecting gases in the laboratory, and in the extraction of gold and silver.

COMPOUNDS OF MERCURY.

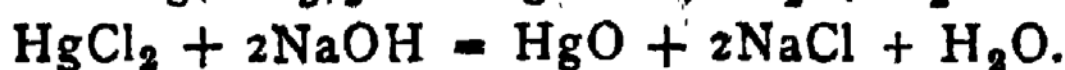
Mercury forms two oxides, but no hydroxide. It also forms two series of salts, called *mercurous* and *mercuric* salts. In the former, mercury behaves like a monad ; in the latter, it acts as a dyad. The vapour and the salts of mercury are poisonous.

Mercurous Oxide, Hg_2O .—Also called *black oxide of mercury*, it is prepared by adding a caustic alkali to the solution of a mercurous salt. For example—



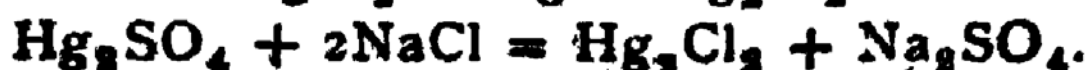
It is changed by heat or light into mercuric oxide and mercury.

Mercuric Oxide, HgO .—Known as *red oxide of mercury*, it is obtained by heating mercury in the air. It is generally prepared (i) by heating mercuric nitrate, or (ii) by adding a caustic alkali to the solution of a mercuric salt (*e.g.* mercuric chloride), when the oxide is obtained as an orange-yellow precipitate.



Mercurous Chloride, HgCl .—It is generally known as *calomel*, and occurs in nature as *horn mercury*. It is manufac-

tured by subliming an intimate mixture of mercuric chloride and mercury, or a mixture of mercurous sulphate and common salt :

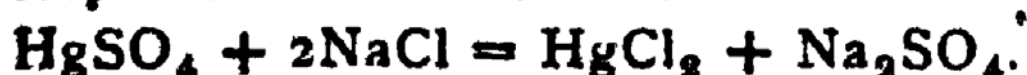


It may also be prepared by precipitating it from a solution of mercurous nitrate by means of hydrochloric acid or common salt :



Mercurous chloride is a white insoluble powder. It is changed by heat or daylight into mercury and mercuric chloride.

Mercuric Chloride, HgCl_2 .—Also called *corrosive sublimate*. It is manufactured by subliming an intimate mixture of mercuric sulphate and common salt :



It may also be prepared by passing chlorine over heated mercury, or by dissolving mercury in *aqua regia*.

It is soluble in water and forms white crystals. When a clean strip of copper is dipped in its solution, mercury is deposited on the copper. Mercuric chloride is a powerful poison and a valuable antiseptic.

Mercurous Sulphate, Hg_2SO_4 .—It may be prepared by triturating mercuric sulphate with mercury. It forms white crystals which are slightly soluble.

Mercuric Sulphate, HgSO_4 .—It is prepared by heating mercury with strong sulphuric acid. (See above). It is a white powder, and is decomposed by water with the formation of a yellow basic sulphate (Hg_2SO_6) known as *Turpeth mineral*.

Mercuric Sulphide, HgS .—This is found in nature in the mineral *cinnabar*. It is obtained as a black amorphous powder by triturating mercury and sulphur or by passing sulphuretted hydrogen into a solution of mercuric chloride. When the black powder is sublimed we finally get red crystals of mercuric sulphide, known as the pigment *vermilion*.

Tests for Mercury.

Dry Reactions.—1. When mercury compounds are heated with sodium carbonate or lime in a dry test tube, globules of

Tests for Iron.

Dry Reaction.—A salt of iron, when heated on a borax-bead, becomes yellowish white in the oxidizing flame, and olive green in the reducing flame.

Wet Reactions :—

	<i>With Ferric Salts</i>	<i>With Ferrous Salts.</i>
1. Alkalies give	Greenish precipitate of ferrous hydrate, turning reddish brown.	Reddish brown precipitate of ferric hydrate.
2. Potassium ferrocyanide gives	A precipitate white at first, but afterwards turning light blue.	A fine blue precipitate (Prussian blue).
3. Potassium ferricyanide ,	A dark blue precipitate (Turnbull's blue).	Brown colouration : but no precipitate.
4. Potassium thiocyanate ,	No colouration (if the ferrous salt is pure).	Dark blood-red colouration.

University Examination Questions.

1. Name the principal ores of iron. How is the metal extracted from these? State the principal uses of the three forms of this metal for various industrial purposes [C. 1911].

2. What are the chief ores of Iron? How is pig-iron obtained from its ores? [A. 03, 04]. How is iron extracted from its ores? [C. 98 ; A. 05, 08].

What weight of iron can theoretically be obtained from 160 tons of hæmatite? [C. 98]. What weight of iron can be obtained from 10 tons of ore containing 25 per cent. of Fe_2O_3 ? [A. 03].

3. What is a blast furnace? Make a sketch of one and describe any manufacturing process in which a blast furnace is used [A. 06].

4. Describe the properties of steel, wrought iron, and cast iron. How is the latter manufactured? Give a sketch with details of the furnace used. [A. 1913]. Describe the properties of Pig-iron, Wrought iron, and Steel. How is the latter commonly manufactured? [A. 1911]. How may cast-iron be converted into wrought-iron and steel? [A. 05].

Describe the Bessemer process for converting cast-iron into steel. In what way is the process modified if the iron contains much phosphorus? What is 'spiegeleisen' used for? [A. 1914].

5. State the chief physical and chemical properties of iron [A. 08].

6. How would you prepare the *hydroxides* and *chlorides* of iron? Give the tests you would employ to distinguish *ferrous* and *ferric* salts. [C. 1913].

7. Mention a laboratory experiment in which ferrous sulphate is obtained as a by-product. Give the equation involved. How is ferrous sulphate obtained in the pure state? State its properties and uses. [C. 1916].

CHAPTER XXXV.

COPPER.

SYMBOL Cu. ATOMIC WEIGHT 63.6.

Occurrence.—Copper occurs native near Lake Superior, in China and in Japan. Its chief ores are—(1) *copper pyrites*, a double sulphide of copper and iron, CuFeS_2 ; (2) *cuprite* or *ruby copper*, consisting of cuprous oxide, Cu_2O ; and (3) *malachite*, a double carbonate and hydrate of copper, $\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_3$.

Extraction.—Copper is generally extracted from copper

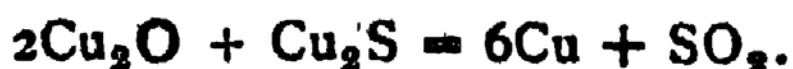


Fig. 50.

pyrites, in which silica, arsenic and other impurities are always present. The process of extraction is briefly this:—The ore is first roasted in a reverberatory furnace (Fig. 50),

and then fused with sand at a high temperature: by this means some impurities are burnt off, whilst the two products cuprous sulphide and silicate of iron are separated from each other. The coarse cuprous sulphide is again roasted and fused, till all the iron of the ore is removed as silicate. By further roasting

of the cuprous sulphide, a portion of it is converted into cuprous oxide; this oxide now interacts with the unoxidized sulphide, producing metallic copper and sulphur dioxide—



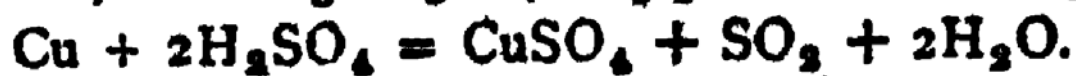
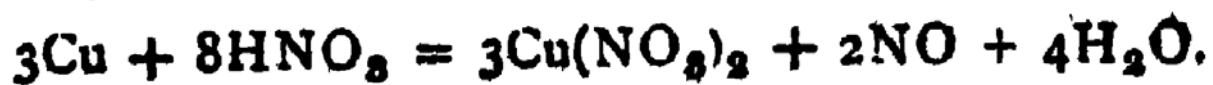
Refining.—The metal is then refined by first melting it and then stirring with poles of green wood, after throwing on the molten mass a quantity of powdered coal or charcoal.

Chemically pure copper is now prepared electrolytically from crude copper. Thick plates of crude copper and thin sheets of the pure metal are alternately suspended in a solution of copper sulphate. On connecting the crude plates with the positive pole and the pure sheets with the negative pole of a dynamo current, pure copper is deposited on the thin sheets, while an equivalent quantity of the crude plates is eaten away.

Properties : Physical.—Copper is a hard lustrous metal having a distinctive red colour. It is very malleable and ductile, and is a very good conductor of heat and electricity. It is nearly 9 times heavier than water. Copper forms very useful alloys.

Chemical.—Copper remains unchanged at ordinary temperatures in dry air. But in moist air it becomes coated with a green layer of basic copper carbonate. When strongly heated in the air, it is converted into black cupric oxide. A solution of common salt and vegetable acids attack copper, forming green salts which are poisonous; hence the danger of using copper vessels for domestic purposes. Copper is deposited from solutions of its salts by an electric current and by iron and zinc: this property is made use of in electrotyping and copper-plating.

Action of Acids on copper.—Hydrochloric acid and dilute sulphuric acid hardly act upon copper. Nitric acid and heated strong sulphuric acid readily act upon it—

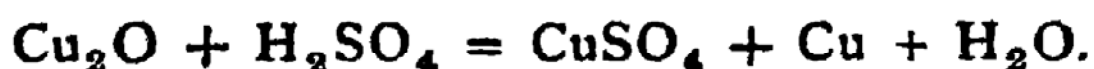


Uses of Copper: Alloys.—Copper is used as electric cables and conductors, for covering wooden ships, in electrotyping, &c. It forms valuable alloys, viz., (1) *Brass*—containing 2 parts copper and 1 part zinc; (2) *Dutch metal* and *Muntz-metal*—containing less copper than brass; (3) *Bell-metal*, *bronze*, and *gun-metal*—containing 8 to 9 parts copper and 2 to 1 part tin; (4) *German silver*—containing copper, zinc, and nickel. Copper is also contained in coins.

OXIDES AND HYDROXIDE OF COPPER.

Copper forms two oxides, both of which are basic and exist in nature—

Cuprous Oxide, Cu_2O .—This is *red oxide of copper*. It may be prepared by gently heating powdered copper in contact with the air. It is generally prepared by boiling a mixed solution of copper sulphate, grape-sugar, and caustic soda or potash. Hydrochloric acid and nitric acid act upon it to produce cuprous chloride and cupric nitrate respectively, and dilute sulphuric acid converts it into copper sulphate and metallic copper.



Cupric Oxide, CuO .—This is *black oxide of copper*. It is prepared by strongly heating copper in air, or by gently heating the nitrate, the carbonate, or the hydrate of the metal—



Cupric oxide is reduced to the metallic state, when heated in a current of hydrogen or carbon monoxide. Its chief use is in the analysis of carbon compounds, which when heated with it are converted into carbon dioxide and water.

Cupric Hydrate, CuH_2O_2 .—It is obtained as a pale blue precipitate by adding caustic soda or potash to copper sulphate solution. When the hydrate is boiled in its mother-liquor, cupric oxide is formed—



It forms with a solution of ammonia a deep blue liquid.

SALTS OF COPPER.

Like mercury and iron, copper forms two series of salts, called *cuprous* and *cupric* salts. The former are changed by oxidation into the latter. The cupric salts are used in pyrotechny for producing coloured flames. Cuprous salts are nearly white.

Cuprous Chloride Cu_2Cl_2 .—It may be prepared by dissolving cuprous oxide in hydrochloric acid. It is generally obtained as a white precipitate by pouring into water a boiled solution of cupric oxide, hydrochloric acid, and copper. This salt is insoluble in water; but it dissolves in ammonia and hydrochloric acid to produce solutions which turn blue by exposure to air.

Cupric Chloride, CuCl_2 .—It is obtained as a brown powder when copper is burnt in chlorine, and as a green solution when cupric oxide or carbonate is dissolved in hydrochloric acid. On evaporating the solution, green crystals of the salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) are formed. Cupric chloride is soluble in water, and is converted by heat into cuprous chloride.

• **Cupric Sulphate**, $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$.—Also known as *blue vitriol*. It is prepared by the action of hot strong sulphuric acid on copper, or by roasting cupric sulphide (CuS) in air. It forms blue crystals, which, when heated lose water and become colourless. The anhydrous salt again becomes blue by contact with water, and is therefore used as a test for the detection of water in liquids. Copper sulphate is used in the preparation of pigments, in electroplating, &c.

Cupric Nitrate, $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$.—It is prepared by the action of nitric acid on copper. It forms blue soluble crystals. It is a powerful caustic and oxidizing agent.

Tests for Copper.

Dry Reactions.—1. A copper salt heated on charcoal, with sodium carbonate, in the reducing flame, yields a red globule of copper.

2. A copper salt heated on a platinum wire, imparts a green colour to the flame.

3. A copper salt heated on a borax bead becomes red in the reducing flame; while in the oxidising flame, it is green when hot and blue when cold.

Wet Reactions.—1. When a piece of bright steel or zinc is immersed in an acid solution of a copper salt, it is soon covered with a deposit of metallic copper.

2. When sulphuretted hydrogen is passed into an acidulated solution of a copper salt, a black precipitate (of CuS) is produced, which is soluble in nitric acid.

3. Solution of ammonia gives a greenish blue precipitate (of CuH_2O_2) which dissolves in excess of ammonia and forms a deep blue solution.

4. Solution of caustic soda or potash gives a light blue precipitate (of CuH_2O_2), which turns black on boiling the mixture.

5. Potassium ferrocyanide gives a reddish brown precipitate (of copper ferrocyanide).

University Examination Questions.

1. What is the chief ore of copper, and how is the metal obtained from it. State the principal uses to which metallic copper is put. What weight of copper can be obtained from 100 grams of an ore containing 50 per cent. of cuprous sulphide? [A. 01].

2. Describe the process for the extraction of copper from its (sulphide) ores. How would you purify ordinary copper so as to give it its maximum tenacity, ductility, and conductivity? [A. 09].

3. Describe the process in use for obtaining copper from its ores. Give an account of the properties of the metal and the modes of formation of its oxides and sulphate [A. 1911].

4. Compare the action of nitric and sulphuric acids on metallic copper. Give equations. What analogy is there between the two reactions? [C. 95].

5. There are two oxides of copper; how can they be prepared from a solution of copper sulphate? What are their properties? [A. 1912].

6. How would you prepare specimens of the two *oxides* and *chlorides* of copper? Compare their properties. [C. 1912, 16]. How could the percentage of copper be estimated in the case of one of the oxides? [C. 1912].

APPENDIX.
IDENTIFICATION OF GASES.
TABLE I.—OF GASES HAVING MARKED ODOUR.

<i>Gas.</i>	<i>Odour</i>	<i>Colour</i>	<i>Heavier or lighter than air</i>	<i>Solubility in water</i>	<i>Combustibility</i>	<i>Confirmatory Tests.</i>
Cl	Irritating	Greenish-yellow	Heavier	Partly soluble	Supports combustion	Bleaches vegetable colours. Liberates iodine from KI.
HCl	Pungent	Colourless	"	Extremely soluble—solution acid	Does not burn, does not support combustion	Fumes in moist air. Forms with NH_3 white fumes of NH_4Cl
NH_3	Ammoniacal	"	Lighter	Extremely soluble—solution alkaline	Burns when surrounded with oxygen	Forms white fumes with HCl. Gives brown tint with Nessler solution.
C_2H_2	Disagreeable	"	Equally heavy	Partly soluble	Burns with a smoky luminous flame	Burns to produce CO_2 .
H_2S	Of rotten eggs	"	Heavier	"	Burns with a bluish flame	Gives black stain on paper moistened with lead acetate.
SO_2	Suffocating	"	"	Highly soluble—solution acid	Does not burn, does not support combustion	Bleaches vegetable colours. Its solution gives a white precipitate with BaCl_2 .

TABLE II.—OF COLOURLESS AND ODOURLESS GASES.

Gas.	Physiological Effect.	Heavier or lighter than air.	Solubility in water.	Combustibility.	Confirmatory Tests.
H	Non-poisonous.	Lightest body.	Insoluble.	Burns with a pale blue flame.	Burns to produce H_2O .
CO	Poisonous.	Lighter	Slightly soluble.	"	{ Burns to produce CO_2 , which turns lime- water milky. Absorbed by solution of Cu_2Cl_2 .
CH_4	Non-poisonous	"	"	Burns with a non-lumi- nous pale flame.	{ Burns to produce CO_2 , Its mixture with O or air explodes on ignition.
C_2H_4	"	Equally heavy.	"	Burns with a luminous smoky flame.	<i>Ditto.</i> Forms an oily liquid with Cl.
O	Supporter of respiration.	Heavier.	"	Supports combustion.	Forms ruddy fumes with NO.
N_2O	Induces laughter and in- sensitivity.	"	"	"	Produces no change with NO.
N	Non-poisonous.	Lighter.	Insoluble.	Does not burn, does not support combustion.	Does not turn limewater milky.
NO	Poisonous	Heavier.	"	<i>Ditto.</i> But burning phos- phorus burns in it.	Forms brown fumes with O.
CO_2	Non-poisonous, but suffocating.	"	Partly soluble.	<i>Ditto.</i> But burning mag- nesium burns in it.	Turns limewater milky.

TABLE OF SOLUBILITY OF SALTS IN WATER.

	Sodium	Potassium	Ammonium	Calcium	Strontium	Barium	Magnesium	Zinc	Mercury (ous)	Mercury (ic)	Aluminium	Lead	Iron	Copper
Chloride	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Chlorate	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Nitrate	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sulphate	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Sulphide	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Carbonate	s	s	s	s	s	s	s	s	s	s	s	s	s	s
Phosphate	s	s	s	s	s	s	s	s	s	s	s	s	s	s

s = Soluble.

s' = Decomposed by water.

s = Slightly soluble.

s = Insoluble (or not known).

QUALITATIVE ANALYSIS.

Qualitative Analysis means the examination of bodies in order to detect their constituents. There are two distinct methods of examining metals or their salts : one is the *dry way* in which experiments are made on the substance without dissolving it ; the other is the *wet way*, in which experiments are performed on the substance in solution. These two kinds of tests supplement each other.

Dry Reactions.—For preliminary examination by the dry way, the substance is first powdered and then a small quantity of it is heated in the blowpipe flame. The examination involves four operations :—

- (1) Heating in a test tube or a bulb tube.
- (2) Heating on a piece of charcoal.
- (3) Heating in a borax bead, prepared by fusing borax on a loop of platinum wire.
- (4) Flame colouration produced by heating the substance on a platinum wire moistened with HCl.

The following are examples of dry reactions :—

I. Heated in a glass tube—

- | | |
|-----------------------------|---------------------------|
| (1) Ammonia evolved | ... Ammonium salts. |
| (2) Brown gases evolved | ... Bromides or Nitrates. |
| (3) Violet gases evolved | ... Iodides. |
| (4) Liquid globules sublime | ... Mercury. |

II. Heated on Charcoal—

- | | |
|--|----------------------------|
| (1) Substance deflagrates | ... Nitrates or Chlorates. |
| (2) Residue is yellow when hot,
white when cold | ... Zn. |
| (3) Residue heated with
$\text{Co}(\text{NO}_3)_2$ giving | |
| Blue mass | ... Al. |
| Pink .. | ... Mg. |
| Green .. | ... Zn. |

- (4) Heated with Na_2CO_3 gives
 (a) White malleable bead with
 yellow incrustation ... Pb.
 (b) Red malleable bead with
 black coating ... Cu.

III. Heated in Bcrax Bead—

- | | | |
|----|--|-------|
| 1. | { In oxidizing flame, green when hot
and blue when cold : | } Cu. |
| | { In reducing flame, red streaks. | |
| 2. | { In oxidizing flame, pale yellow : | } Fe. |
| | { In reducing flame, olive green. | |

IV. Flame Colourations—

- | | |
|-------------------|-------------|
| (1) Green | ... Ba, Cu. |
| (2) Crimson | ... Sr. |
| (3) Orange red | ... Ca. |
| (4) Orange yellow | ... Na. |
| (5) Violet | ... K. |

• **Wet Reactions**—Examination by the wet way is more elaborate, and consists in observing the reactions of the substance with different reagents.

• The first step is to prepare a solution of the substance. The solid is powdered and dissolved in boiling water. The insoluble residue is boiled with nitric acid and after evaporation to dryness the mass is dissolved in water. The two solutions of the salts being then mixed together, we have to proceed as follows in order to identify the metals contained in the mixture :

I. Add HCl to the solution.—White precipitate may contain AgCl, PbCl₂, Hg₂Cl₂. [Keep filtrate A].

• Wash the precipitate and add NH_4OH in excess—

Precipitate dissolves ... Ag.

„ is blackened ... Hg(ous)—With KI, greenish.

„ is unaltered ... Pb „ „ yellow.

II. Pass H_2S through filtrate A.—Black precipitate indicates HgS, PbS, CuS, Bi₂S₃; coloured precipitates indicate other metals. [Keep filtrate B].

Wash the black precipitate, and (after digesting with NaOH or KOH) boil with HNO_3 —

Black precipitate	...HgS.
Blue solution	...Cu—With NH_4OH , deep blue.
Colourless solution	...Pb or Bi.

III. (a) Add NH_4Cl and NH_4OH to filtrate B or to the original solution.—Brown precipitate indicates $\text{Fe}(\text{HO})_3$, white precipitate indicates $\text{Al}(\text{HO})_3$. [Keep filtrate C].

(b) Add $(\text{NH}_4)_2\text{S}$ or pass H_2S through filtrate C.—White precipitate indicates ZnS . [Keep filtrate D].

IV. Add $(\text{NH}_4)_2\text{CO}_3$ to filtrate D.—White precipitate may contain CaCO_3 , SrCO_3 , BaCO_3 ; solution may contain Mg, K, Na.

Test precipitate in the dry way by observing flame colouration.

To one portion of the solution add Na_2HPO_4 .—White precipitate indicates Mg. To another portion of the solution add HCl and PtCl_4 and stir.—Yellow precipitate indicates K. Presence of Na is detected by flame colouration.

[For confirmatory reactions see *Tests* below the respective metals].

University Examination Questions.

I

1. How would you identify each of the following gases :—nitrous oxide, nitric oxide, hydrogen, carbon monoxide, marsh gas? [C. 96].

2. Make a list of the colourless gases with which you are acquainted. You are given several jars of a certain colourless gas; describe carefully, in order, the experiments which you would make for the purpose of identifying it [C. 97].

3. Give definite experiments by means of which you can distinguish between the contents of six gas jars containing respectively :—oxygen, nitric oxide, sulphur dioxide, carbon dioxide, chlorine and hydrogen chloride [C. 1900].

4. How would you distinguish between the following pairs of gases :—(a) bromine vapour and nitrogen peroxide, (b) oxygen

and nitrous oxide, (c) marsh gas and carbon monoxide, (d) hydrogen sulphide and nitrogen? [C. 01].

5. You are given four bottles containing respectively Oxygen, Hydrogen, Nitrogen and Carbon Dioxide. How could you determine the identity of the various gases? [A. 04].

6. Give a chemical method of distinguishing between the following gases :—(a) Hydrogen and carbon monoxide, (b) Hydrogen chloride and sulphur dioxide, (c) Oxygen and nitrous oxide, (d) Nitrogen and carbon dioxide. [C. 07].

7. Three cylinders are given to you full of colourless invisible gases which may be oxygen, or nitrous oxide, or nitric oxide. How would you identify them? [C. 1911].

8. You are given three cylinders fitted with a colorless gas, soluble in water, which may be sulphur dioxide, hydrochloric acid, or ammonia. How would you prove what the gas is? [C. 1914].

9. State any points of resemblance between the following substances and enumerate differences in their properties by means of which they can be distinguished and identified :—Cl, CO, SO₂, NO₂, N₂O. [A. 99].

10. You are given four jars filled respectively with N, NO, N₂O, and CO. How would you by experiment find out definitely which was which? [A. 07].

11. You are given three jars of each of the following gases :—H₂, O₂, N₂, N₂O, CO, CO₂, C₂H₂, C₂H₄, and CH₄. Give definite experiments by means of which you could distinguish between them. [A. 1914].

II

1. How would you satisfy yourself whether a given white solid is chlorate of potash, ammonium nitrate, or oxalic acid? [C. 04].

2. Give one test for each of the following substances :—(a) Nitrates, (b) Sulphates, (c) Chlorides, (d) Sulphites, (e) Nitrites, (f) Carbonates. [C. 08].

3. By what test or tests would you distinguish a nitrite from a nitrate [A. 09, 13], a sulphite from a sulphate [A. 1910, 13], a chlorate from a chloride [A. 13], a ferrous salt from a ferric salt? [A. 13].

4. How would you identify the metals contained in the following substances by dry reactions (*i. e.* before the blowpipe, &c)?

Give details of the operations :—(a) zinc sulphate, (b) mercuric chloride, (c) nitrate of copper. [C. 10].

5. A solid substance being given to you which might either be a salt of zinc or mercury, how would you proceed to identify it? [C. 13].

6. A colourless solution of a substance is given to you. You are told that it is a chloride or a sulphate of one of the following metals :—mercury, copper, iron, calcium, or sodium. How would you proceed to identify the dissolved substance? [C. 10].

MISCELLANEOUS QUESTIONS.

1. Explain fully the following terms, and describe one experiment to illustrate your answer in each case :—(a) synthesis, (b) analysis, (c) crystallisation; (d) deliquescence [C. 1910].

2. Explain the following terms :—(a) catalysis, (b) water of crystallisation, (c) efflorescence, (d) reduction, (e) sublimation. Illustrate by examples [C. 1911].

3. Explain the following terms, giving examples in illustration of your answers :—(a) double decomposition, (b) saturated solution, (c) freezing mixture, (d) indicator, (e) nascent state [C. 08]; (a) Compound radicles, (b) nascent state, (c) oxidizing agent, (d) catalysis, and (e) deliquescence. [A. 1914].

4. Define atom, nascent state, acid, electrolysis, allotropy [A.04].

5. Write concise explanatory notes on the following :—(a) deliquescence, (b) anhydrous, (c) crystal, (d) fluorspar, (e) oil of vitriol [C. 03].

6. Classify the following oxides, stating the reasons :—Sulphur trioxide, carbon monoxide, nitric oxide, calcium oxide, mercuric oxide. How would you identify them? [C. 1916].

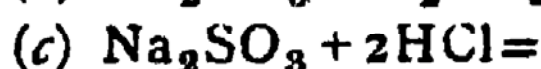
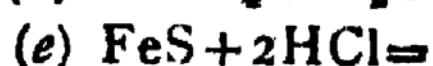
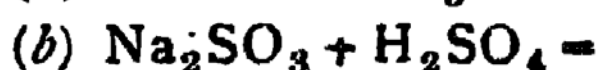
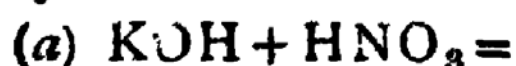
7. Give the chemical names and formulæ of—sand, lime, hæmatite, saltpetre, calcspar, caustic soda, iron pyrites, blue vitriol, aqua regia, diamond [A. 01].

8. What are the chemical names and molecular formulæ of the following :—Oil of vitriol, Glauber's salts, Muriatic acid, Nitre, Laughing gas, Fire damp? [C. 07].

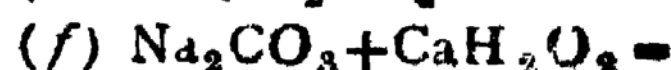
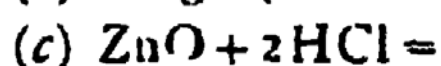
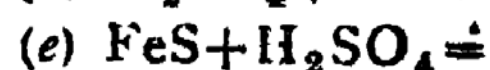
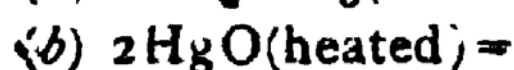
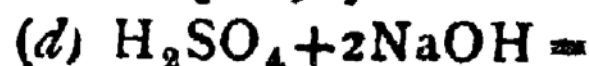
9. Give the chemical names, formulæ, and uses of the following substances :—(a) oil of vitriol, (b) sal-ammoniac, (c) bleaching powder, (d) plaster of Paris. What happens when water is added to each of these substances ? [C. 1912].

10. Give the *chemical names, formulae, and uses* of—(a) green vitriol ; (b) gypsum ; (c) Chili saltpetre ; (d) Epsom salts. What is the action of heat on these substances. [C. 1915].

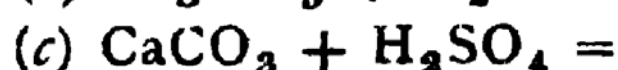
11. Complete the following equations, and in each case describe the physical and chemical phenomena which occur :—[C. 91].



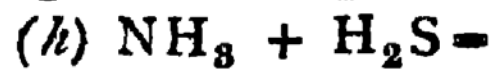
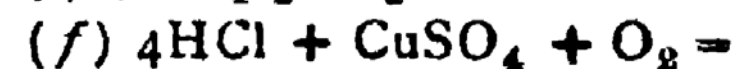
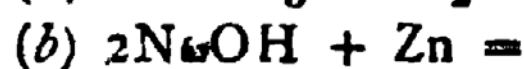
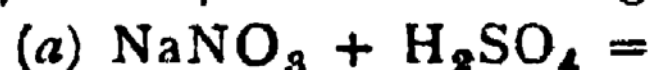
12. Complete the following equations :—[C. 98].



13. Complete the following equations, stating briefly the physical and chemical changes that accompany each reaction :—[C. 1900].



14. Complete the following equations :—[C. 91].



15. Describe fully the chemical changes, if any, which occur (a) when dry potassium chlorate is intimately mixed with black oxide of manganese ; (b) when the same mixture is boiled with water ; (c) when copper oxide is mixed with charcoal and strongly heated ; (d) when oxalic acid is heated with sulphuric acid. Express chemical changes by equations [C. 93].

16. Write equations to represent the chemical reactions which occur when (1) sodium sulphite is heated with hydrochloric acid ; (2) slaked lime and sal-ammoniac are heated together ; (3) oxalic acid is heated with strong sulphuric acid ; (4) a warm concentrated solution of caustic potash is treated with chlorine. [C. 96].

17. Write equations to represent the reactions which occur

when—(a) Ammonium nitrate is heated ; (b) Steam is passed over very hot coal ; (c) Sulphuric acid is treated with ammonia ; (d) Carbon dioxide is passed into limewater. [C. 97].

18. Describe the reactions in words and give equations representing what takes place when (a) marsh gas is completely burnt in air, (b) magnesium ribbon is burnt in oxygen, (c) phosphorus is burnt in chlorine. [C. 01].

19. Describe the action of water or steam on the following substances :—sodium, magnesium, iron, copper, and charcoal. [A. 05].

20. What happens when the following substances are heated strongly ?—(a) Ammonium nitrite, (b) Lead nitrite, (c) Sulphuric acid. Give equations for any change which occurs, and name the products. [C. 06].

21. Describe the action of heat on the following substances, giving equations :—(a) Potassium chlorate, (b) Potassium nitrate, (c) Ammonium nitrate, (d) Sulphuric acid, (e) Carbonate of lime. [C. 08].

22. What changes do the following undergo when heated—Potassium carbonate, sodium nitrate, barium sulphate, copper nitrate ferrous sulphate, and crystallized magnesium chloride ? [A. 1913].

23. What is the action of heat on — KHCO_3 , KNO_3 , K_2SO_4 , KHSO_4 , KClO_4 , and $\text{K}_2\text{Mn}_2\text{O}_8$? [A. 1915].

24. Describe fully the changes that you will observe in the following cases :—(a) A two-annas piece is thrown into nitric acid ; (b) A bit of phosphorus is thrown into a jar of chlorine ; (c) A few drops of strong solution of ammonia are introduced into a jar containing hydrochloric acid gas ; (d) Sulphuretted hydrogen is passed into a solution of blue vitriol ; (e) Carbonic acid gas is passed into lime water ; (f) A mixture of nitric oxide gas and carbon disulphide vapour is ignited. [C. 07].

25. Describe, with equations, the changes, both physical and chemical, that take place in the following cases :—(a) A two-anna piece is thrown into nitric acid, (b) Carbon monoxide gas is passed over ferric oxide heated in a hard glass tube, (c) Some copper nitrate is strongly heated in a dish, (d) A discoloured oil-painting is washed over with dilute hydrogen peroxide, (e) Oxalic acid is heated with strong sulphuric acid. [A. 1915].

26. What gases are produced by the action of strong sulphuric acid on each of the following substances (with the aid of heat)?—
(a) Metallic copper, (b) Formic acid, (c) Sodium chloride. Give equations. Describe how you would collect the gases and compare their physical and chemical properties. [C. 09].

27. What happens when (a) chlorine is passed through caustic potash solution, (b) sulphur dioxide is passed through iodine solution, (c) strong sulphuric acid is heated with sulphur, (d) caustic soda solution is added to dilute sulphuric acid? [C. 1911].

28. How would you obtain (a) carbon from carbon dioxide, (b) bromine from hydrobromic acid, and (c) mercury from a solution of mercuric chloride? Describe the process you would employ in each case and give equations of the reactions that take place. [C. 1912].

29. Represent by equations the reactions occurring between:—
(a) oil of vitriol and Chili saltpetre, (b) nitric acid and copper, (c) barium dioxide and oil of vitriol, (d) quicklime and sal-ammoniac, (e) oil of vitriol and fluor-spar. [A. 97].

30. Explain the reactions that take place when the following substances react on one another, and give the chemical equations:—(a) Potassium nitrate and sulphuric acid, (b) Manganese dioxide and hydrochloric acid, (c) Copper and nitric acid, (d) Chlorine and ammonia. [A. 04].

31. Write equations showing the following reactions:—(a) sulphuric acid with copper, (b) nitric acid with copper, (c) sulphuric acid with zinc, (d) caustic soda with phosphorus, (e) caustic soda with chlorine gas. Which of the above need heat to cause a reaction to take place? Do any react differently in the hot from the manner in which they react in the cold? [A. 06].

32. The following substances are separately treated with sulphuric acid:—copper, zinc, potassium chloride, sodium carbonate, and manganese dioxide. State with equations the reactions which take place. [A. 02].

33. What is the action of caustic soda on (a) yellow phosphorus, (b) metallic zinc, (c) chlorine, (d) calcium acetate, and (e) copper sulphate? State briefly the conditions necessary for the action you describe and give the names of all the substances formed. [A. 1914].

34. How would you make the following substances? Compare

their physical characters, and describe the effects of dilute hydrochloric acid on each :—(a) caustic soda, (b) magnesium sulphate, (c) zinc oxide, (d) mercuric sulphide. Indicate the chief uses of caustic soda and zinc oxide. [C. 09.]

35. How are the following substances ordinarily prepared? What are their chemical and physical properties, and what are the changes effected in them by heat? By what tests would you identify them?—(a) calomel, (b) slaked lime, (c) green vitriol, (d) blue vitriol. [C. 09].

36. How would you ordinarily prepare the following substances? Give their formulas, and describe their physical and chemical properties, and give one test for each—(a) laughing gas; (b) bleaching powder; (c) ferric chloride; (d) Glauber's salt. [C. 1910].

37. Give the formulæ and method of preparation of (a) Potassium nitrate, (b) Sodium carbonate, (c) Calcium chloride. By what simple tests might they be distinguished? [A. 08].

38. How are caustic soda, potassium carbonate, copper oxide, and lead acetate prepared? [A. 05].

39. How would you prepare the following substances in a pure condition?—(a) calcium carbonate from calcium chloride, (b) ferrous chloride from ferric chloride, (c) copper oxide from copper sulphate, (d) lead sulphate from lead acetate. [A. 1913].

40. How would you prepare (a) anhydrous magnesium chloride, (b) calomel, and (c) sulphate of iron (crystalline)? Give one test for the metallic radicle in each of the above. [C. 1914].

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